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TITLE: DISPERSION OF ETHYLENE-BASED POLYMER
COMPOSITION AND ITS
USE

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide an aqueous dispersion of an ethylene-based polymer composition, an organic solvent dispersion of an ethylene-based polymer composition and an additive for a printing ink that impart a performance having both excellent wear resistance and excellent blocking resistance to an aqueous ink and an oily ink.

SOLUTION: The aqueous dispersion of an ethylene-based polymer composition is produced by dispersing, in water, particles of an ethylene-based polymer composition comprising (A) an ethylene-based polymer having an Mn in a range of 400-8,000, an Mw/Mn of 3 or less and a relationship between a crystallization

temperature and a density which satisfies a specified formula and (B)
a
modified ethylene-based polymer being modified with an unsaturated
carboxylic
acid or its derivative or with a sulfonate wherein the content of the
unsaturated carboxylic acid or its derivative is a concentration of
30-100
mgKOH as determined by a KOH titration method per gram of the
modified polymer
or the content of the sulfonate is 0.1-50 millimole equivalents in
terms of -SO

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the additive for printing ink with which the additive for printing ink with which the particle of an ethylene system polymer constituent consists of an ethylene system polymer constituent aqueosity dispersing element which water comes to distribute, and this aqueosity dispersing element, the additive for printing ink which consists of the above-mentioned particle, and the above-mentioned particle consist of an ethylene system polymer constituent organic solvent dispersing element which a hydrocarbon solvent comes to distribute, and this organic solvent dispersing element in more detail about an ethylene system polymer constituent dispersing element and its application.

[0002]

[Background of the Invention] Only by the resin used as the principal component, although water color ink has been conventionally used widely as printing ink to corrugated paper etc., since abrasion resistance is low, it is mainly adding waxes and has given abrasion resistance. this invention person has already proposed the aqueosity dispersing element of the low-molecular-weight polyolefine which does not contain a low-molecular-weight surfactant in this application (refer to JP,58-42207,B and JP,5-156028,A).

[0003] However, the approach of drying printed matter under an elevated temperature is being circulated so that offset rotation ink may see in recent years. On the other hand, in order to make abrasion resistance discover, the thing of an elasticity system tends to be crushed by the front face of an ink layer, and a wax is powerful. In the aqueosity dispersing element of the waxes mainly used conventionally, to double abrasion resistance and blocking resistance sufficient after drying under an elevated temperature, and to make it discovered by elasticity-ization of a wax, since the lack of BUROKINGU-proof by the increment in tuck nature of a wax occurs is demanded.

[0004] On the other hand, the organic solvent with which the distributed solvent of a wax does not contain toluene like alcohol, ethyl acetate, and aliphatic hydrocarbon, either may be used from solvent use regulation according [oily printing ink] to an environmental problem. However, a wax is a poor solvent which is generally hard to dissolve in these solvents, it is one side, and the so-called crystallization method for carrying out soluble [of the wax] at an elevated temperature, and obtaining a crystallization article by addition of cooling conditions or the further poor solvent is difficult.

[0005]

[Objects of the Invention] engine-performance ***** having the abrasion resistance and the blocking resistance this invention excelled [blocking resistance] in ink -- it aims at offering the additive for printing ink with which the additive for printing ink with which the particle [like] of an ethylene system polymer constituent consists of an ethylene system polymer constituent aqueosity dispersing element which water comes to distribute, and an aqueosity dispersing element, the additive for printing ink which consist of the above-mentioned particle, and the above-mentioned particle consist of an ethylene system polymer constituent organic solvent dispersing element which a hydrocarbon solvent

comes to be distributed, and this organic solvent dispersing element.

[0006]

[Summary of the Invention] The following ethylene system polymer constituent aqueosity dispersing elements, an ethylene system polymer constituent organic solvent dispersing element, and the additive for printing ink are offered by this invention.

(1) The relation between the crystallization temperature (a part for 2-degree-C/in Tc (degree C) and temperature fall rate) which it is (A) ethylene homopolymerization, or ethylene / alpha olefin copolymer, and the number average molecular weight (Mn) measured with gel permeation chromatography (GPC) is in the range of 400-8,000, and Mw/Mn is three or less, and was measured with the differential scanning calorimeter (DSC), and the consistency (D (kg/m³)) measured with the density gradient tube method is the following type (1).

$0.501xD-366 \geq Tc \text{ -- (1)}$

It is the denaturation ethylene system polymer to which the ***** ethylene system polymer, and (B) ethylene homopolymerization, or ethylene / alpha olefin copolymer denaturalized with unsaturated carboxylic acid, its derivative, or sulfonate. The amount of denaturation in unsaturated carboxylic acid or its derivative by KOH titration conversion Per [30] 1g of denaturation polymers - 100mgKOH, or the amount of denaturation in sulfonate by -SO₃-conversion The ethylene system polymer constituent aqueosity dispersing element by which water comes to distribute the particle of the ethylene system polymer constituent which consists of a denaturation ethylene system polymer which is 0.1 to 50 millimol per 1g of denaturation polymers.

(2) An ethylene system polymerization body composition object aqueosity dispersing element given in (1) by which the above-mentioned ethylene system polymer (A) is compounded with a metallocene catalyst.

(3) (1) which has the weight ratio (A/B) of the above-mentioned ethylene system polymer (A) and the above-mentioned denaturation ethylene system polymer (B) in the range of 95 / 5 - 50/50, or an ethylene system polymerization body composition object aqueosity dispersing element given in (2).

(4) An ethylene system polymer constituent aqueosity dispersing element given in either of (1) - (3) which has a consistency by the density gradient tube method in the range of 850 - 920 kg/m³, and has the above-mentioned ethylene system polymer (A) in the range whose volume mean diameter of the particle of an ethylene system polymer constituent is 0.1-20 micrometers.

(5) Additive for printing ink which becomes either of (1) - (4) from the ethylene system polymer constituent aqueosity dispersing element of a publication.

(6) Additive for printing ink which becomes either of (1) - (4) from the particle of the ethylene system polymer constituent of a publication.

(7) Ethylene system polymer constituent organic solvent dispersing element by which a hydrocarbon solvent comes to distribute the particle of an ethylene system polymer constituent given in either of (1) - (4).

The additive for printing ink characterized by being set to (8) and (7) from the ethylene system polymer constituent organic solvent dispersing element of a publication.

[0007]

[Detailed Description of the Invention] The ethylene system polymer constituent aqueosity dispersing element, the ethylene system polymer constituent organic solvent dispersing element, and the additive for printing ink concerning this invention are explained concretely below. Water comes to distribute the particle of the ethylene system polymer constituent with which the ethylene system polymer constituent aqueosity dispersing element of this invention consists of a (A) ethylene system polymer and a (B) denaturation ethylene system polymer.

[0008] First, (A) ethylene system polymer and (B) denaturation ethylene system polymer which are used for the ethylene system polymer constituent aqueosity dispersing element concerning this invention are explained.

(A) The ethylene system polymer (A) used by ethylene system polymer this invention is ethylene homopolymerization, or ethylene / alpha olefin copolymer.

[0009] As an alpha olefin, 1-octene of the propene of the carbon atomic number 3, 1-butene of the carbon atomic number 4, the 1-pentene of the carbon atomic number 5, 1-hexene of the carbon atomic number 6, 4-methyl-1-pentene, and the carbon atomic number 8 etc. is mentioned, and they are a propene, 1-butene, 1-hexene, and 4-methyl-1-pentene preferably here. the number average molecular weight (Mn) which measured the ethylene system polymer (A) with gel permeation chromatography (GPC) -- 400-8,000 -- desirable -- 1000-8000 -- it is in the range of 2000-5000 more preferably.

[0010] When number average molecular weight (Mn) is in above-mentioned within the limits, there is an inclination which is easy to emulsify when distributing a constituent in water, and is easy to distribute in the diameter of a granule. Mw/Mn of an ethylene system polymer (A) is 2.8 or less more preferably 2.9 or less three or less. If Mw/Mn is in above-mentioned within the limits, since a low tail component and a high tail component will decrease, the dispersibility at the time of emulsification improves and there is an inclination which can do a more uniform dispersing element.

[0011] The relation between the crystallization temperature (a part for 2-degree-C/in Tc (degree C) and temperature fall rate) which measured the ethylene system polymer (A) with the differential scanning calorimeter (DSC), and the consistency (D (kg/m³)) measured with the density gradient tube method is the following type (1).

$0.501 \times D - 366 \geq T_c$ -- (1)

It is $0.501 \times D - 366.5 \geq T_c$ preferably. -- (1a)

It is $0.501 \times D - 367 \geq T_c$ more preferably. -- (1b)

If the relation between ***** crystallization temperature and a consistency fills the above-mentioned formula, since it will serve as a narrow ethylene system polymer of comonomer presentation distribution, there is an inclination which serves as low tack nature more.

[0012] Such an ethylene system polymer (A) has few low crystal components at low molecular weight. In other words, since distribution of a comonomer presentation is narrow, it has low tack nature. The ethylene system polymer (A) used by this invention can be manufactured by homopolymerizing ethylene, for example under existence of the following catalysts, or copolymerizing ethylene and an alpha olefin.

[0013] Homogeneous catalysts, such as a metallocene system catalyst which consists of a metallocene compound, and the organic aluminium oxy compound and/or ionization ionicity compound of the transition metals chosen from the vanadium system catalyst which consists of a fusibility vanadium compound and an organoaluminium compound, and the 4th group of a periodic table as a catalyst for obtaining an ethylene system polymer (A), are mentioned. The vanadium system catalyst and the metallocene system catalyst are well-known, for example, as follows.

[0014] (Fusibility vanadium compound) As a fusibility vanadium compound which forms a vanadium system catalyst, the vanadium compound expressed with the following type (2) or (3) is mentioned.

$VO(OR_1)_a X_1 b$ -- (2)

$V(OR_1)_c X_1 d$ -- (3)

As for R₁, a hydrocarbon group and X₁ are halogen atoms among a formula.

[0015] a, b, c, and d are numbers which fill $0 \leq a \leq 3$, $0 \leq b \leq 3$, $2 \leq a+b \leq 3$, $0 \leq c \leq 4$, $0 \leq d \leq 4$, and $3 \leq c+d \leq 4$, respectively. In addition, the electron donor addition product of the fusibility vanadium compound which an electron donor is contacted and is obtained as a fusibility vanadium compound can also be used.

(Organoaluminium compound) As such a compound that can use the compound which has at least one aluminum-carbon to carbon bond for intramolecular as an organoaluminium compound which forms a vanadium system catalyst, it is the organoaluminium compound and m aluminum(R₂) (OR₃)_n H_p X₂q which are expressed with the following general formula (4), for example. -- (4)

(R₂ and R₃ are hydrocarbon groups which may differ even if mutually the same, and usually contain preferably 1-15 carbon atoms [1-4] among a formula.) X₂ is a halogen atom. $0 < m \leq 3$ and n are numbers with which $0 \leq n < 3$ and p fill $0 \leq p < 3$, and q fills $0 \leq q < 3$, and, moreover, m is $m+n+p+q=3$. The ** alkylation object of the 1st group metal and aluminum which are expressed with the following general formula (5) etc. is mentioned.

[0016] (M1) aluminum (R2) -- (5)

(M1 is Li, Na, or K among a formula, and R2 is the same as R2 of said general formula (4).)

(Metallocene compound) The metallocene compound which forms a metallocene system catalyst is a metallocene compound of the transition metals chosen from the 4th group of a periodic table, and the compound expressed with the following general formula (6) as a concrete example is mentioned.

[0017] $M2L_x$ -- (6)

Here, the valence of transition metals M2 and L of the transition metals with which M2 is chosen from the 4th group of a periodic table, and x are ligands. There are a zirconium, titanium, a hafnium, etc. as an example of the transition metals shown by M2. L is a ligand configured in transition metals M2, among those at least one ligand L is a ligand which has a cyclopentadienyl frame, and the ligand which has this cyclopentadienyl frame may have the substituent.

[0018] As a ligand L which has a cyclopentadienyl frame For example, a cyclopentadienyl group, a methylcyclopentadienyl radical, an ethylcyclopentadienyl radical, n- or i-propylcyclopentadienyl radical, n-, i-, sec-, or t-butylcyclopentadienyl radical, A dimethylcyclopentadienyl radical, a methylpropyl cyclopentadienyl group, Alkyl or cycloalkyl substituent cyclopentadienyl groups, such as a methylbutyl cyclopentadienyl group and a methylbenzyl cyclopentadienyl group; an indenyl group, 4, 5 and 6, a 7-tetrahydro indenyl group, a fluorenyl group, etc. are mentioned further. The hydrogen of the radical which has this cyclopentadienyl frame may be permuted by the halogen atom or the trialkylsilyl group.

[0019] When the aforementioned metallocene compound has two or more radicals which have a cyclopentadienyl frame as a ligand L, the radicals which have two cyclopentadienyl frames among those may be combined through permutation silylene radicals, such as permutation alkylene group; silylene radicals, such as alkylene group; isopropylidene, such as ethylene and a propylene, and diphenylmethylenes, or a dimethyl silylene radical, a diphenyl silylene radical, and a methylphenyl silylene radical, etc.

[0020] As ligands L other than the ligand which has a cyclopentadienyl frame (ligand which does not have a cyclopentadienyl frame), the hydrocarbon group, an alkoxy group, an aryloxy radical, a sulfonic-acid content radical (-SO three R4), a halogen atom, or a hydrogen atom (it is here and R4 is the aryl group permuted by an alkyl group, the alkyl group permuted by the halogen atom, the aryl group, the halogen atom, or the alkyl group.) of the carbon atomic numbers 1-12 etc. is mentioned.

[0021] (Example -1 of a metallocene compound) The metallocene compound expressed with the above-mentioned general formula (6) is more specifically expressed with the following general formula (7), when the valence of transition metals is 4.

$R5kR6lR7mR8nM2$ -- (7)

or [that the transition metals with which M2 is chosen from the 4th group of the periodic table, the radical (ligand) on which R5 has a cyclopentadienyl frame, and R6, R7 and R8 have a cyclopentadienyl frame independently here, respectively] -- or it is the radical (ligand) which it does not have. k is one or more integers and is $k+l+m+n=4$.

[0022] The example of the metallocene compound which M2 is a zirconium and contains at least two ligands which have a cyclopentadienyl frame is given to a degree. A bis(cyclopentadienyl) zirconium monochrome RIDOMONO hydride, bis(cyclopentadienyl) zirconium dichloride, a bis(1-methyl-3-butylcyclopentadienyl) zirconium screw (trifluoromethane sulfonate), bis(1, 3-dimethylcyclopentadienyl) zirconium dichloride, etc.

[0023] In the aforementioned compound, at least 1 and 3- can also use the compound with which at least 1 and 2- transposed the substituent cyclopentadienyl group to the substituent cyclopentadienyl group. Moreover, as another example of a metallocene compound, it is the radical (ligand) on which at least two, R5 and R6, of R5, R6, R7, and R8 have a cyclopentadienyl frame in the above-mentioned general formula (7), and the metallocene compound of the bridge type with which this at least two radical is combined through the alkylene group, the permutation alkylene group, the silylene radical, or the permutation silylene radical can also be used. [for example,] At this time, R7 and R8 are the same as that of ligands L other than the ligand which has the cyclopentadienyl frame mentioned above

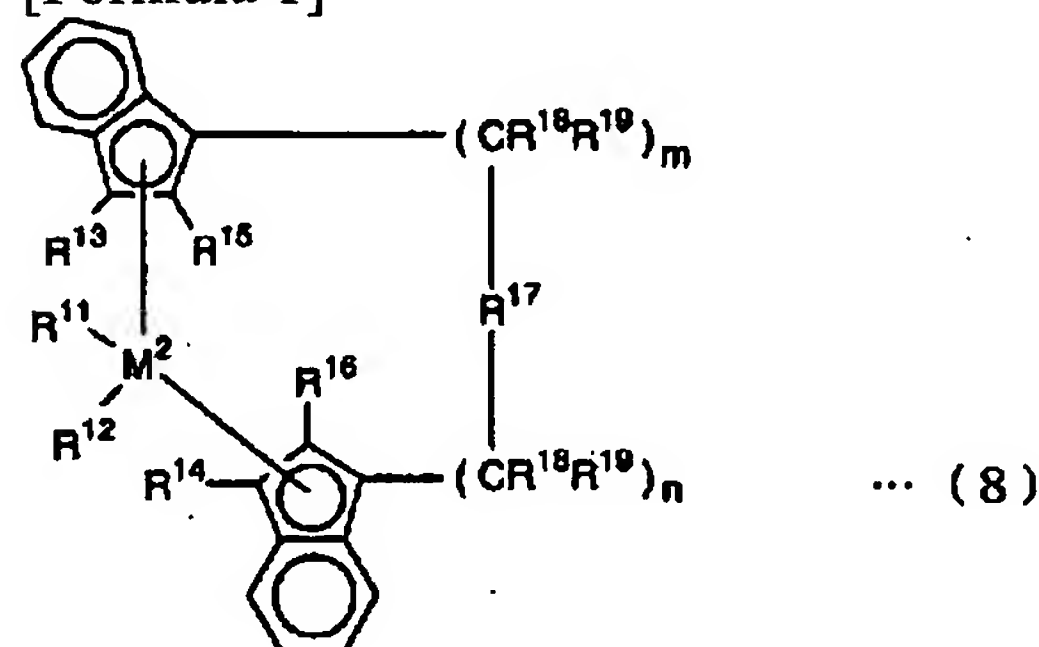
independently respectively.

[0024] As a such bridge type metallocene compound, an ethylene bis(indenyl) dimethyl zirconium, ethylene bis(indenyl) zirconium dichloride, isopropylidene (cyclopentadienyl-fluorenyl) zirconium dichloride, diphenyl silylene bis(indenyl) zirconium dichloride, methylphenyl silylene bis(indenyl) zirconium dichloride, etc. are mentioned.

[0025] (Example -2 of a metallocene compound) As an example of another metallocene compound, the metallocene compound given in JP,4-268307,A expressed with the following general formula (8) is mentioned again.

[0026]

[Formula 1]



[0027] Here, M2 is the 4th group transition metals of the periodic table, and titanium, a zirconium, and a hafnium are specifically mentioned. You may differ, even if R11 and R12 are mutually the same.

Hydrogen atom; Alkyl group [of the carbon atomic numbers 1-10]; Alkoxy group [of the carbon atomic numbers 1-10]; aryl group [of the carbon atomic numbers 6-10]; -- aryloxy radical [of the carbon atomic numbers 6-10]; -- alkenyl radical [of the carbon atomic numbers 2-10]; -- arylated alkyl radical [of the carbon atomic numbers 7-40]; -- alkyl aryl radical [of the carbon atomic numbers 7-40]; -- aryl alkenyl radical [of the carbon atomic numbers 8-40]; -- Or it is a halogen atom and is a chlorine atom preferably.

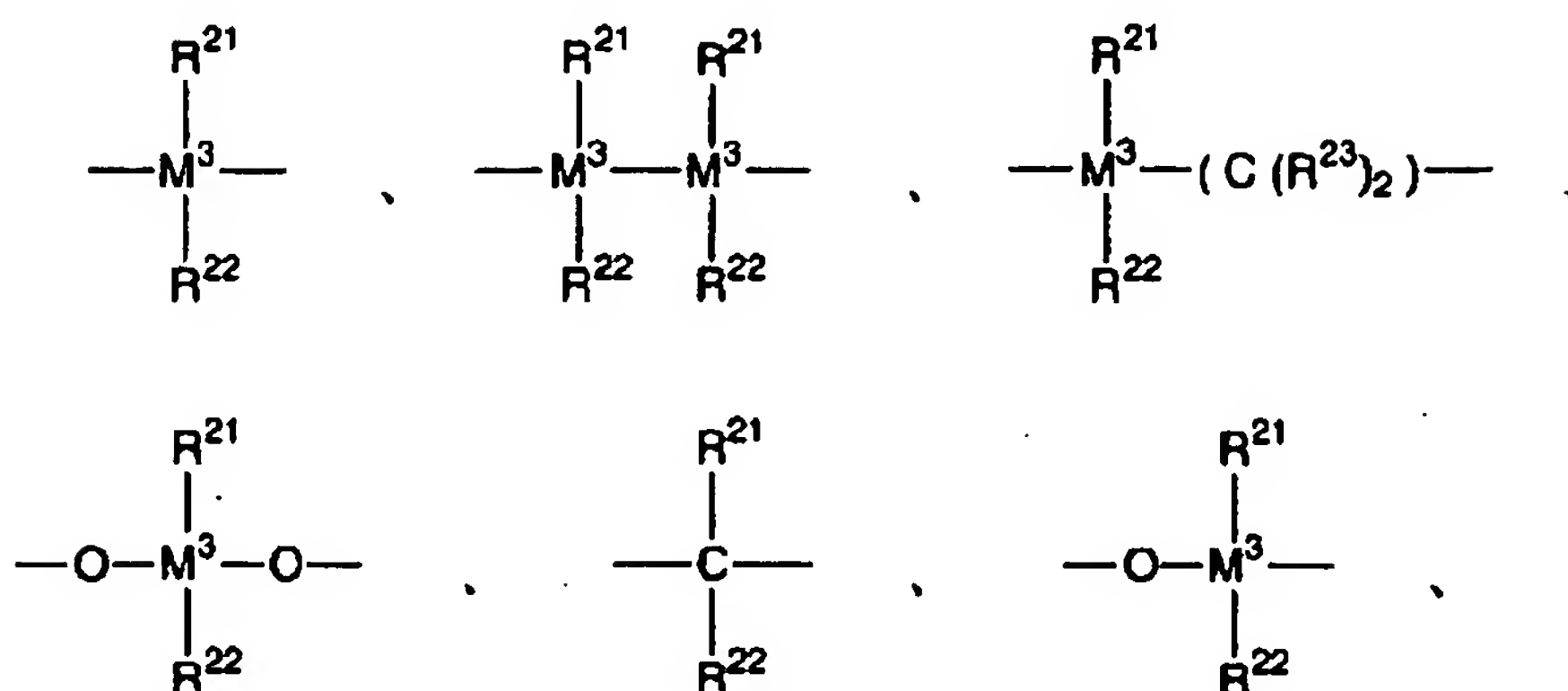
[0028] The alkyl group of the carbon atomic numbers 1-10 of which may differ even if R13 and R14 are mutually the same, and hydrogen atom; halogen atom; halogenation may be done; they are aryl group; -N (R20)2 of the carbon atomic numbers 6-10, -SR20, -OSi (R20)3, -Si (R20)3, or -P(R20) 2 set. here -- R20 -- a halogen atom -- desirable -- the chlorine atom; carbon atomic numbers 1-10 -- desirable -- alkyl group [of 1-3];, or the carbon atomic numbers 6-10 -- it is the aryl group of 6-8 preferably. As for R13 and especially R14, it is desirable that it is a hydrogen atom.

[0029] except for the hydrogen atom, even if R15 and R16 are mutually [it is the same as R13 and R14, and] the same, they may differ from each other, and they are preferably the same. Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, trifluoromethyl, etc. are mentioned to the alkyl group of the carbon atomic numbers 1-4 which may be halogenated, and a concrete target, and R15 and R16 have especially preferably desirable methyl.

[0030] In the above-mentioned general formula (8), R17 is chosen from the following group.

[0031]

[Formula 2]



[0032] = BR²¹, =AlR²¹, -germanium-, -Sn-, -O-, -S-, =SO, =SO₂, =NR²¹, =CO, =PR²¹, =P(O) R²¹, etc. M³ -- silicon, germanium, or tin -- they are silicon or germanium preferably. Even if R²¹, R²², and R²³ are mutually the same, you may differ here. Hydrogen atom; Halogen atom; Alkyl group [of the carbon atomic numbers 1-10]; Fluoro alkyl group [of the carbon atomic numbers 1-10]; aryl group [of the carbon atomic numbers 6-10]; -- fluoro aryl group [of the carbon atomic numbers 6-10]; -- alkoxy group [of the carbon atomic numbers 1-10]; -- alkenyl radical [of the carbon atomic numbers 2-10]; -- the carbon atomic number 7 - 40 arylated-alkyl radical; -- aryl alkenyl radical [of the carbon atomic numbers 8-40]; -- Or it is the alkyl aryl radical of the carbon atomic numbers 7-40. "R²¹ and R²²", or "R²¹ and R²³" may become together with the atom which they combine, respectively, and a ring may be formed.

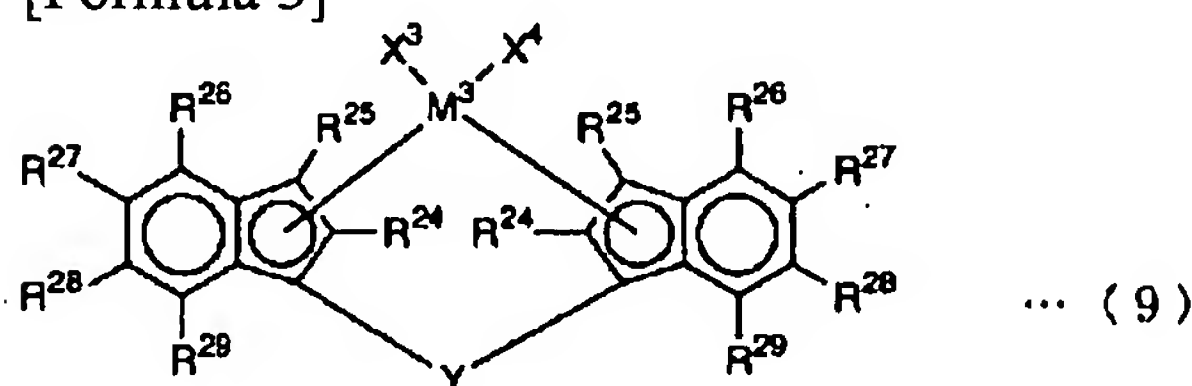
[0033] Moreover, as for R¹⁷, it is desirable that it is =CR²¹R²², =SiR²¹R²², =GeR²¹R²², -O-, -S-, =SO, =PR²¹, or =P(O) R²¹. You may differ, even if R¹⁸ and R¹⁹ are mutually the same, and the same thing as R²¹ is mentioned. even when m and n are mutually the same -- differing -- **** -- respectively -- 0, 1, or 2 -- desirable -- 0 or 1 -- it is -- m+n -- 0, 1, or 2 -- it is 0 or 1 preferably.

[0034] The following compound is mentioned as an example of a metallocene compound expressed with the above-mentioned general formula (8). rac-ethylene (2-methyl-1-indenyl) 2-zirconium dichloride, rac-dimethyl silylene (2-methyl-1-indenyl) 2-zirconium dichloride, etc. These metallocene compounds can be manufactured by the approach of a publication to JP,4-268307,A.

[0035] (Example -3 of a metallocene compound) As a metallocene compound, the metallocene compound expressed with the following general formula (9) can also be used again.

[0036]

[Formula 3]



[0037] Among a formula, M³ shows the transition-metals atom of the 4th group of the periodic table, and is specifically titanium, a zirconium, a hafnium, etc. Even if R²⁴ and R²⁵ are mutually the same, they may differ from each other, and they show the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20, the halogenated hydrocarbon radical of the carbon atomic numbers 1-20, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical.

[0038] As for R²⁴, it is desirable that it is a hydrocarbon group, and it is especially desirable that it is the alkyl group of methyl, ethyl, or the carbon atomic numbers 1-3 of propyl. R²⁵ has hydrogen or a desirable hydrocarbon group, and it is especially desirable that it is the alkyl group of a hydrogen atom or methyl, ethyl, or the carbon atomic numbers 1-3 of propyl. Even if R²⁶, R²⁷, R²⁸, and R²⁹ are mutually the same, they may differ from each other, and they show the hydrocarbon group of a

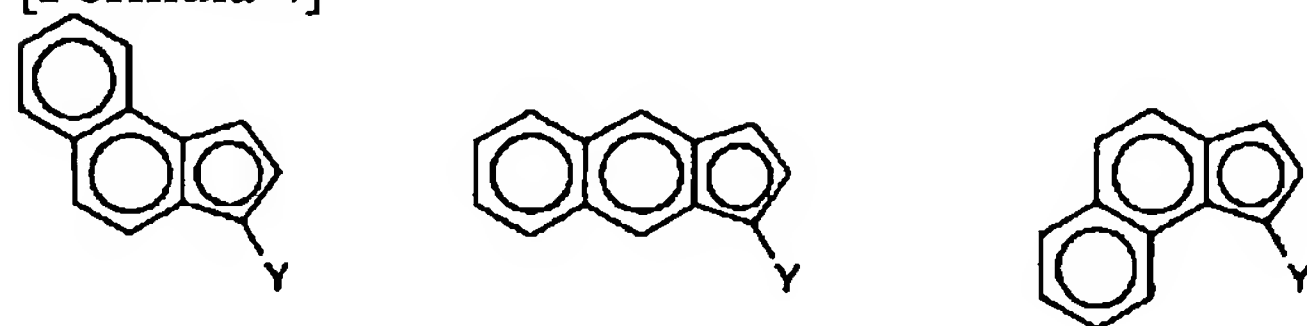
hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20, and the halogenated hydrocarbon radical of the carbon atomic numbers 1-20. In these, it is desirable that they are hydrogen, a hydrocarbon group, or a halogenated hydrocarbon radical. At least one of R26, R27 and R27, and R28, R28 and R29 sets may become together with the carbon atom which they have combined, and they may form the aromatic series ring of a monocycle. Moreover, in a certain case, these may join together mutually and, as for radicals other than the radical which forms an aromatic series ring, a hydrocarbon group or two or more sorts of halogenated hydrocarbon radicals may be annular. In addition, when R29 is substituents other than an aromatic series radical, it is desirable that it is a hydrogen atom.

[0039] You may differ, even if X3 and X4 are mutually the same. A hydrogen atom, a halogen atom, Y which shows the hydrocarbon group of the carbon atomic numbers 1-20, the halogenated hydrocarbon radical of the carbon atomic numbers 1-20, an oxygen content radical, or a sulfur content radical The divalent hydrocarbon group of the carbon atomic numbers 1-20, the divalent halogenated hydrocarbon radical of the carbon atomic numbers 1-20, A divalent silicon content radical, a divalent germanium content radical, a divalent tin content radical, -O-, -CO-, -S-, -SO-, -SO2-, -NR30-, -P(R30)-, -P(O) and (R30)-, -BR30-, or -AlR30- (correcting, R30 is the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20 and the halogenated hydrocarbon radical of the carbon atomic numbers 1-20) is shown.

[0040] In the aforementioned formula, what is expressed with a degree type is mentioned as a ligand which at least one of R26, R27 and R27, and R28, R28 and R29 sets configures in M3 including the aromatic series ring of the monocycle which combines mutually and is formed.

[0041]

[Formula 4]

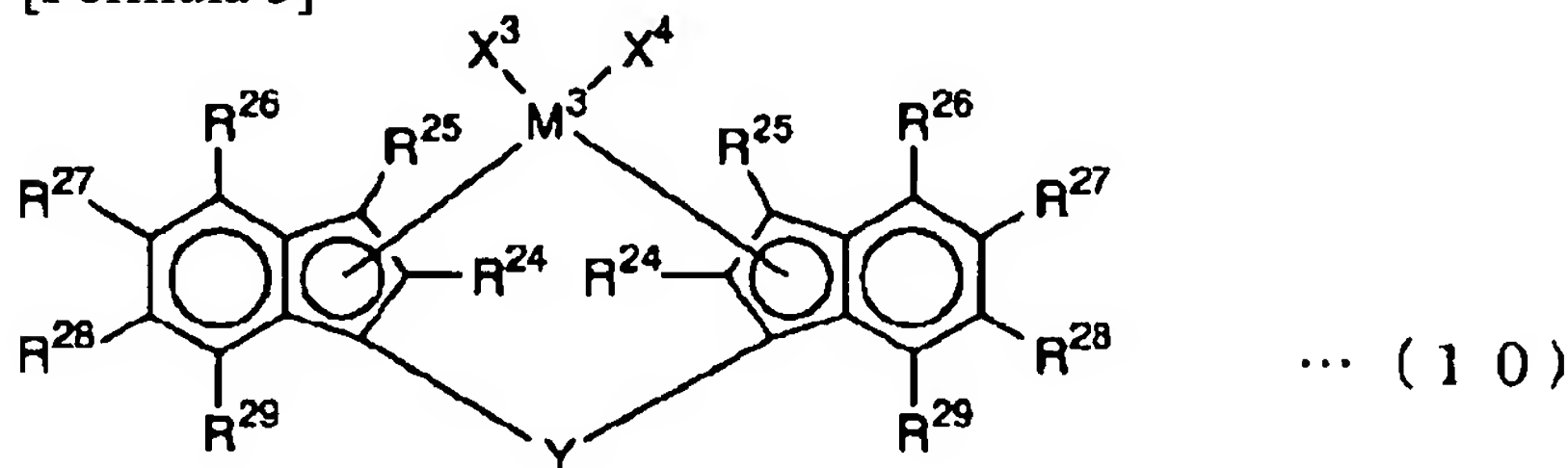


[0042] (Y is the same as what was shown in the front type among a formula.)

(Example -4 of a metallocene compound) As a metallocene compound, the metallocene compound expressed with the following general formula (10) can also be used.

[0043]

[Formula 5]



[0044] M3, R24, R25, R26, R27, R28, and R29 are the same as what was used by the above-mentioned general formula (9) among a formula. It is desirable that two radicals which contain R26 among R26, R27, R28, and R29 are alkyl groups, and it is desirable that R26, R28, or R28 and R29 are an alkyl group. As for this alkyl group, it is desirable that it is the 2nd class or the 3rd class alkyl group.

Moreover, this alkyl group may be permuted by the halogen atom and the silicon content radical, and the substituent illustrated by R24 and R25 is mentioned as a halogen atom and a silicon content radical.

[0045] As for radicals other than an alkyl group, it is desirable among R26, R27, R28, and R29 that it is a hydrogen atom. Moreover, two sorts of radicals chosen from these may join together mutually, and R26, R27, R28, and R29 may form the monocycle or many rings other than an aromatic series ring. As a halogen atom, the same thing as the above R24 and R25 is mentioned.

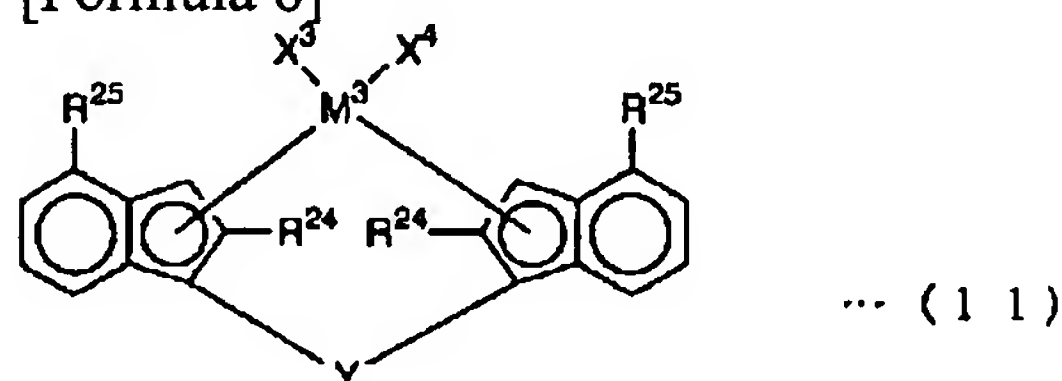
[0046] The same thing as the above is mentioned as X3, X4, and Y. The concrete example of a metallocene compound expressed with the above-mentioned general formula (10) is shown below. rac-dimethyl silylene-bis(4, 7-dimethyl-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2, 4, 7-trimethyl-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2, 4, 6-trimethyl-1-indenyl) zirconium dichloride, etc.

[0047] In these compounds, the transition-metals compound which transposed the zirconium metal to the titanium metal and the hafnium metal can also be used. Although a transition-metals compound is usually used as racemic modification, an R form or a smooth S form can also be used for it.

(Example -5 of a metallocene compound) As a metallocene compound, the metallocene compound expressed with the following general formula (11) can also be used.

[0048]

[Formula 6]



[0049] The same atom or the same radical is mentioned among a formula with the above-mentioned general formula (9) having explained M3, R24, X3, X4, and Y. As for R24, it is desirable that it is a hydrocarbon group, and it is especially desirable that it is the alkyl group of methyl, ethyl, propyl, or the carbon atomic numbers 1-4 of butyl. R25 shows the aryl group of the carbon atomic numbers 6-16. As for R25, it is desirable that they are phenyl and naphthyl. The aryl group may be permuted by the hydrocarbon group of a halogen atom and the carbon atomic numbers 1-20, or the halogenated hydrocarbon radical of the carbon atomic numbers 1-20.

[0050] As X3 and X4, it is desirable that it is the hydrocarbon group of a halogen atom and the carbon atomic numbers 1-20. The concrete example of a metallocene compound expressed with the above-mentioned general formula (11) is shown below. rac-dimethyl silylene-bis(4-phenyl-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2-methyl-4-phenyl-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2-methyl-4-(alpha-naphthyl)-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2-methyl-4-(beta-naphthyl)-1-indenyl) zirconium dichloride, rac-dimethyl silylene-bis(2-methyl-4-(1-anthryl)-1-indenyl) zirconium dichloride, etc. Moreover, in these compounds, the transition-metals compound which transposed the zirconium metal to the titanium metal or the hafnium metal can also be used.

[0051] (Example -6 of a metallocene compound) The metallocene compound expressed with the following general formula (12) can also be used as a metallocene compound again.

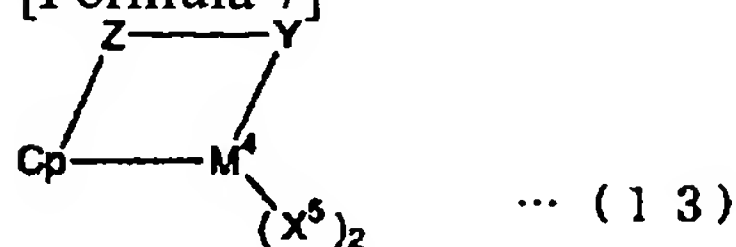
LaM 4X52 -- (12)

Here, M4 is the metal of the 4th group of a periodic table, or the lanthanide series. La is the derivative of a delocalization pi-bonding radical, and is a radical which has given the restricted geometry configuration to the metal M4 active site. X5 is a gel mill radical which may differ even if mutually the same, and contains a hydrogen atom, a halogen atom, a 20 or less carbon atomic number hydrocarbon group, the silyl radical containing 20 or less silicon, or 20 or less germanium.

[0052] In this compound, the compound shown by the degree type is desirable.

[0053]

[Formula 7]



[0054] M4 is titanium, a zirconium, or a hafnium. X5 is the same as that of what was explained by the

above-mentioned general formula (12). Cp is a substituent cyclopentadienyl group which is carrying out pi bonding to M4, and has Substituent Z. Z is oxygen, sulfur, boron, or the element (for example, silicon, germanium, or tin) of the 4th group of a periodic table.

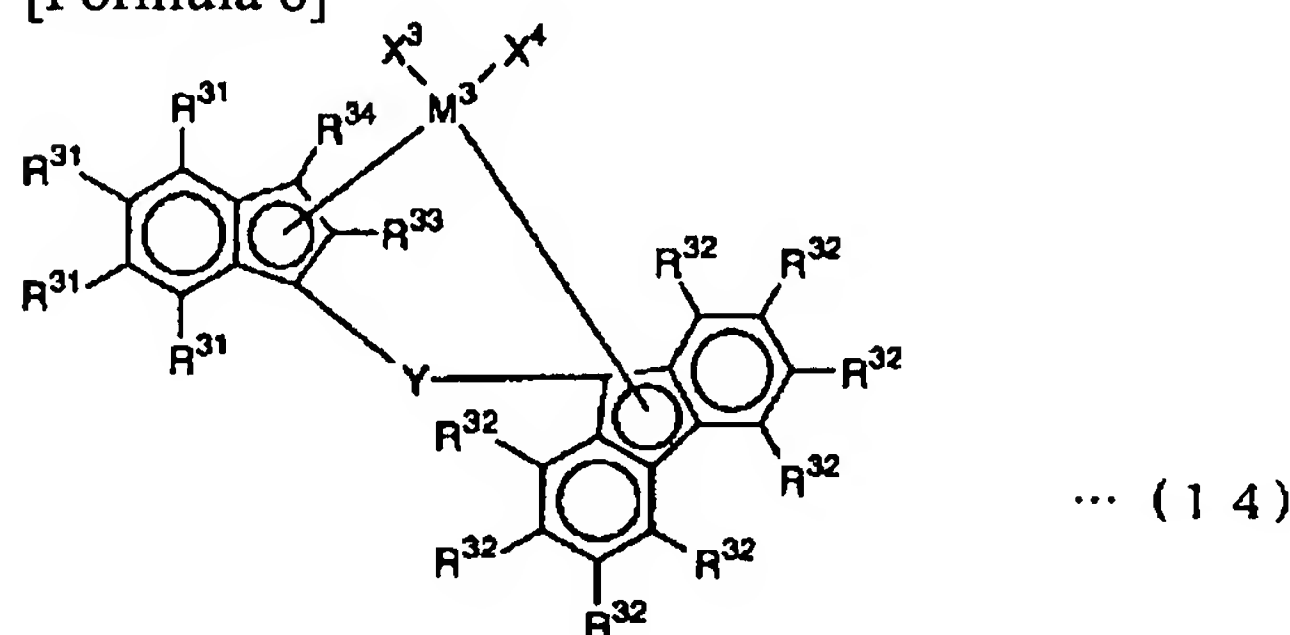
[0055] Y is a ligand containing nitrogen, Lynn, oxygen, or sulfur, and may form the condensed ring by Z and Y. The concrete example of a metallocene compound expressed with such a formula is shown below. (Dimethyl (t-butyl amide) (tetramethyl-eta5-cyclopentadienyl) silane) Titanium dichloride, titanium dichloride (-(tetramethyl (t-butyl amide)-eta5-cyclopentadienyl) 1, 2-ethane diyl), etc.

Moreover, in this metallocene compound, the compound which transposed titanium to the zirconium or the hafnium can also be mentioned.

[0056] (Example -7 of a metallocene compound) As a metallocene compound, the metallocene compound expressed with the following general formula (14) can also be used again.

[0057]

[Formula 8]



[0058] It is the transition-metals atom of the 4th group of the periodic table, and M3 is titanium, a zirconium, or a hafnium, and, specifically, is a zirconium preferably. You may differ, even if R31 is mutually the same. At least one or more pieces The aryl group of the carbon atomic numbers 11-20, The arylated alkyl radical of the carbon atomic numbers 12-40, the aryl alkenyl radical of the carbon atomic numbers 13-40, At least two radicals which are the alkyl aryl radical or silicon content radical of the carbon atomic numbers 12-40, or adjoin among the radicals shown by R31 form an unit, two or more aromatic series rings, or an aliphatic series ring with those carbon atoms to combine. In this case, carbon atomic numbers are 4-20 as a whole including the carbon atom with which R31 combines the ring formed of R31.

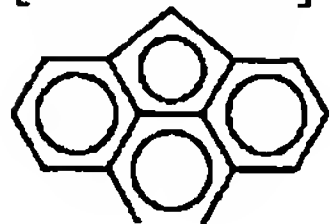
[0059] R31 other than R31 which form an aryl group, an arylated alkyl radical, the aryl alkenyl radical, the alkyl aryl radical and the aromatic series ring, and the aliphatic series ring is the alkyl group or silicon content radical of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10. Even if R32 is mutually the same, it may differ, and it is the alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10, the aryl group of the carbon atomic numbers 6-20, the alkenyl radical of the carbon atomic numbers 2-10, the arylated alkyl radical of the carbon atomic numbers 7-40, the aryl alkenyl radical of the carbon atomic numbers 8-40, the alkyl aryl radical of the carbon atomic numbers 7-40, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical.

[0060] Moreover, at least two radicals which adjoin among the radicals shown by R32 may form an unit, two or more aromatic series rings, or an aliphatic series ring with those carbon atoms to combine. In this case, R32 other than R32 in which carbon atomic numbers are 4-20, and form the aromatic series ring and the aliphatic series ring as a whole including the carbon atom with which R32 combines the ring formed of R32 is the alkyl group or silicon content radical of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10.

[0061] In addition, the mode which becomes the structure [like a degree type] whose fluorenyl group is is also contained in the radical which two radicals shown by R32 consist of by forming an unit, two or more aromatic series rings, or an aliphatic series ring.

[0062]

[Formula 9]



[0063] As for R32, it is desirable that they are a hydrogen atom or an alkyl group, and it is especially desirable that it is the hydrocarbon group of a hydrogen atom or methyl, ethyl, and the carbon atomic numbers 1-3 of propyl. As a fluorenyl group which has R32 as such a substituent, a 2 and 7-dialkyl-fluorenyl group is raised as a suitable example, and the alkyl group of the carbon atomic numbers 1-5 is mentioned as 2 in this case, and an alkyl group of 7-dialkyl. Moreover, even if R31 and R32 are mutually the same, they may differ.

[0064] You may differ, even if R33 and R34 are mutually the same. The same hydrogen atom as the above, The alkyl group of a halogen atom and the carbon atomic numbers 1-10, the aryl group of the carbon atomic numbers 6-20, They are the alkenyl radical of the carbon atomic numbers 2-10, the arylated alkyl radical of the carbon atomic numbers 7-40, the aryl alkenyl radical of the carbon atomic numbers 8-40, the alkyl aryl radical of the carbon atomic numbers 7-40, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical. As for R33 and R34, it is [among these] desirable that at least one side is the alkyl group of the carbon atomic numbers 1-3.

[0065] Even if X3 and X4 are mutually the same, they may differ from each other, and they are the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20, the halogenated hydrocarbon radical of the carbon atomic numbers 1-20, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the conjugated diene residue formed from X3 and X4. As conjugated diene residue formed from X3 and X4, the residue of 1,3-butadiene, 2, 4-hexadiene, 1-phenyl-1,3-pentadiene, 1, and 4-diphenyl butadiene is desirable, and such residue may be further permuted by the hydrocarbon group of the carbon atomic numbers 1-10.

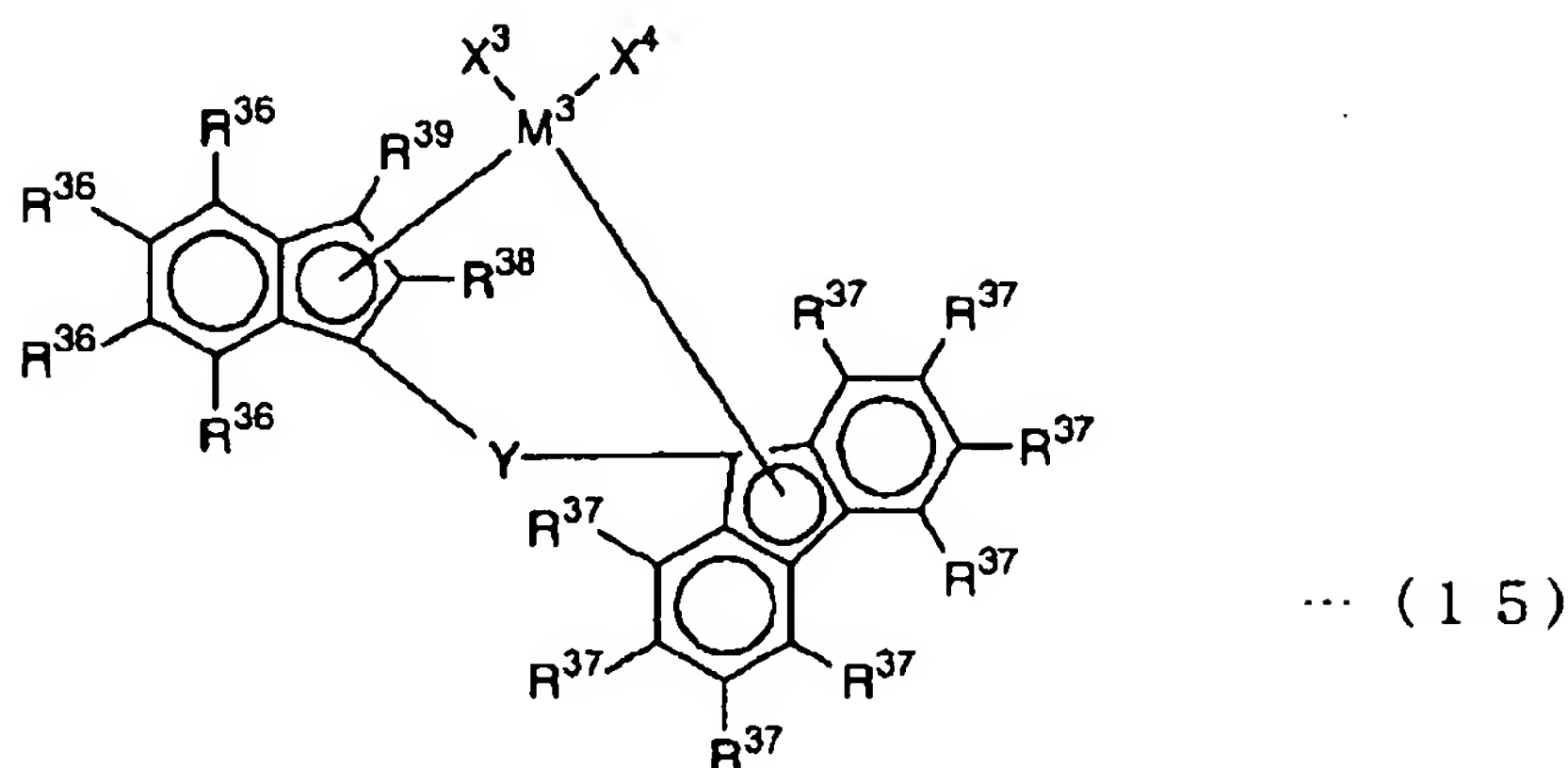
[0066] As X3 and X4, it is desirable that it is the hydrocarbon group or sulfur content radical of a halogen atom and the carbon atomic numbers 1-20. Y The divalent hydrocarbon group of the carbon atomic numbers 1-20, the divalent halogenated hydrocarbon radical of the carbon atomic numbers 1-20, A divalent silicon content radical, a divalent germanium content radical, a divalent tin content radical, -O-, -CO-, -S-, -SO-, -SO2-, -NR35-, -P(R35)-, -P(O) and (R35)-, -BR35-, or -AlR35- (correcting, R35 is the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20 and the halogenated hydrocarbon radical of the carbon atomic numbers 1-20) is shown.

[0067] That by which the shortest connection section of -Y- is constituted by one piece or two atoms also among these divalent radicals is desirable. Moreover, R35 is the hydrocarbon group of a halogen atom and the carbon atomic numbers 1-20, and the halogenated hydrocarbon radical of the carbon atomic numbers 1-20. It is desirable that it is the hydrocarbon group, the divalent divalent silicon content radical, or the divalent divalent germanium content radical of the carbon atomic numbers 1-5, as for Y, it is more desirable that it is a divalent silicon content radical, and it is desirable that they are especially alkyl silylene, alkyl aryl silylene, or aryl silylene.

[0068] (Example -8 of a metallocene compound) As a metallocene compound, the metallocene compound expressed with the following general formula (15) can also be used again.

[0069]

[Formula 10]



[0070] Among a formula, M3 is the transition-metals atom of the 4th group of the periodic table, is specifically titanium, a zirconium, or a hafnium, and is a zirconium preferably. Even if R36 is mutually the same, it may differ, and it is the alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10, the aryl group of the carbon atomic numbers 6-10, the alkenyl radical of the carbon atomic numbers 2-10, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical. In addition, the above-mentioned alkyl group and the alkenyl radical may be permuted by the halogen atom.

[0071] As for R36, it is desirable that they are an alkyl group, an aryl group, or a hydrogen atom, and it is [among these] especially desirable that they are an aryl group or hydrogen atoms, such as a hydrocarbon group of the carbon atomic numbers 1-3 of methyl, ethyl, n-propyl, and i-propyl, phenyl, alpha-naphthyl, and beta-naphthyl. Even if R37 is mutually the same, it may differ, and it is the alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10, the aryl group of the carbon atomic numbers 6-20, the alkenyl radical of the carbon atomic numbers 2-10, the arylated alkyl radical of the carbon atomic numbers 7-40, the aryl alkenyl radical of the carbon atomic numbers 8-40, the alkyl aryl radical of the carbon atomic numbers 7-40, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical. In addition, the halogen may permute the above-mentioned alkyl group, an aryl group, the alkenyl radical, the arylated alkyl radical, the aryl alkenyl radical, and the alkyl aryl radical.

[0072] As for R37, it is desirable that they are a hydrogen atom or an alkyl group, and it is [among these] especially desirable that it is the hydrocarbon group of the carbon atomic numbers 1-4 of a hydrogen atom or methyl, ethyl, n-propyl, i-propyl, n-butyl, and tert-butyl. Moreover, even if said R36 and R37 are mutually the same, they may differ. Either of R38 and R39 is the alkyl group of the carbon atomic numbers 1-5, and another side is the alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10, the alkenyl radical of the carbon atomic numbers 2-10, a silicon content radical, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the Lynn content radical.

[0073] Either of R38 and R39 is the alkyl group of the carbon atomic numbers 1-3, such as methyl, ethyl, and propyl, and, as for another side, it is [among these] desirable that it is a hydrogen atom. Even if X3 and X4 are mutually the same, they may differ from each other, and they are the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20, the halogenated hydrocarbon radical of the carbon atomic numbers 1-20, an oxygen content radical, a sulfur content radical, a nitrogen content radical, or the conjugated diene residue formed from X3 and X4. It is [among these] desirable that it is the hydrocarbon group of a halogen atom or the carbon atomic numbers 1-20.

[0074] Y The divalent hydrocarbon group of the carbon atomic numbers 1-20, the divalent halogenated hydrocarbon radical of the carbon atomic numbers 1-20, A divalent silicon content radical, a divalent germanium content radical, a divalent tin content radical, - O-, -CO-, -S-, -SO-, -SO2-, -NR40-, - P (R40)-, -P(O) and (R40)-, -BR40-, or -AlR40- (correcting, R40 is the hydrocarbon group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-20 and the halogenated hydrocarbon radical of

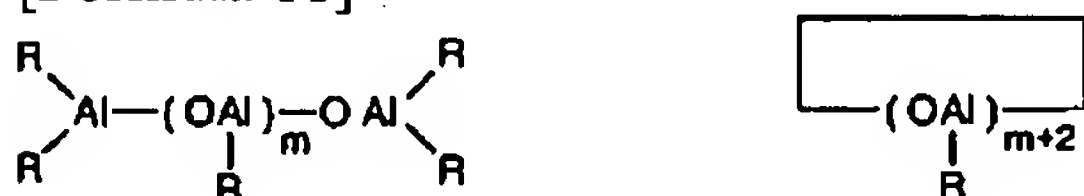
the carbon atomic numbers 1-20) is shown.

[0075] It is desirable that it is the hydrocarbon group, the divalent silicon content radical, or the divalent germanium content radical of the carbon atomic numbers 1-5, as for Y, it is more desirable that it is a divalent silicon content radical, and it is [among these] desirable that they are especially alkyl silylene, alkyl aryl silylene, or aryl silylene. The metallocene compound explained above is independent, or is combined two or more sorts and used. Moreover, a metallocene compound may be diluted and used for a hydrocarbon or halogenated hydrocarbon.

[0076] (Organic aluminium oxy compound) An organic aluminium oxy compound may be well-known alumino oxan, and may be an organic aluminium oxy compound of benzene insolubility. Such well-known alumino oxan is specifically expressed with a degree type.

[0077]

[Formula 11]



[0078] here -- R -- hydrocarbon groups, such as a methyl group, an ethyl group, a propyl group, and butyl, -- it is -- desirable -- a methyl group and an ethyl group -- it is a methyl group especially preferably and m is the integer of 5-40 preferably two or more. alumino oxan may be formed from the mixed alkyloxy aluminum unit which consists of an alkyloxy aluminum unit (here -- it is -- R' and R' -- ' -- the same hydrocarbon group as R -- it can illustrate -- R' and R' -- ' -- difference -- a radical is expressed.) expressed with the alkyloxy aluminum unit and formula (OAl (R'')) which are expressed with a formula (OAl (R')). In addition, the organic aluminium oxy compound may contain the organic compound component of metals other than a small amount of aluminum.

[0079] (Ionization ionicity compound) As an ionization ionicity compound (called an ionicity ionization compound and an ionicity compound), Lewis acid, an ionicity compound, a borane compound, and a carborane compound can be illustrated. As Lewis acid, the compound expressed with BR₃ (R is the phenyl group or fluorine which may have substituents, such as a fluorine, a methyl group, and a trifluoromethyl radical.) is mentioned. As a concrete thing of Lewis acid, trifluoro boron, triphenyl boron, tris (4-fluoro phenyl) boron, tris (3, 5-difluoro phenyl) boron, tris (4-fluoro methylphenyl) boron, tris (pentafluorophenyl) boron, tris (p-tolyl) boron, tris (o-tolyl) boron, tris (3, 5-dimethylphenyl) boron, etc. are mentioned.

[0080] As said ionicity compound, trialkyl permutation ammonium salt, N, and N-dialkyl anilinium salt, dialkyl ammonium salt, a thoria reel HOSUFONIUMU salt, etc. are mentioned. As trialkyl permutation ammonium salt as an ionicity compound, triethyl ammonium tetrapod (phenyl) boron, TORIPURO pill ammonium tetrapod (phenyl) boron, Tori (n-butyl) ammonium tetrapod (phenyl) boron, etc. are mentioned. As dialkyl ammonium salt as an ionicity compound, JI (1-propyl) ammonium tetrapod (pentafluorophenyl) boron, dicyclohexyl ammonium tetrapod (phenyl) boron, etc. are mentioned.

[0081] As said ionicity compound, triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N, and N-dimethyl anilinium tetrakis (pentafluorophenyl) borate, ferro SENIUMU tetrapod (pentafluorophenyl) borate, etc. can also be mentioned. As said borane compound, the salt of metal borane anions, such as decaborane (9); screw [Tori (n-butyl) ammonium] nona borate, screw [Tori (n-butyl) ammonium] deca borate, and screw [Tori (n-butyl) ammonium] bis(dodeca hydride dodeca borate) nickel acid chloride (III), etc. is mentioned.

[0082] As said carborane compound, the salt of metal carborane anions, such as 4-cull BANONA borane (9), 1, 3-JIKARUBA nona borane (8) screw [Tori (n-butyl) ammonium] bis(undecahydride-7-KARUBA undeca borate) nickel acid chloride (IV), etc. is mentioned. Such an ionization ionicity compound is independent, or is combined two or more sorts and used. Moreover, said carrier compound can be made to be able to support an organic aluminium oxy compound and an ionization ionicity compound, and they can also be used.

[0083] Moreover, it faces forming a metallocene system catalyst and the organoaluminium compound

described above with the organic aluminium oxy compound and/or the ionization ionicity compound may be used.

(Polymerization) The ethylene system polymer (A) used by this invention carries out copolymerization of other monomers which usually homopolymerize ethylene by the liquid phase under existence of the above-mentioned vanadium system catalyst or a metallocene system catalyst, or are copolymerized according to ethylene, an alpha olefin, and the need. Under the present circumstances, although a hydrocarbon solvent is generally used, an alpha olefin may be used as a solvent. In addition, each monomer used here is as having mentioned above.

[0084] It is 140 degrees C or more in the vapor phase polymerization which carries out a polymerization without using the suspension polymerization and solvent which carry out a polymerization in the condition that an ethylene system polymer (A) exists as a particle in solvents, such as a hexane, and polymerization temperature, and the solution polymerization which carries out a polymerization after the ethylene system polymer (A) has fused by the solvent, coexistence, or independent is possible for a polymerization method, and it is desirable by both sides of economical efficiency and quality also in it. [of solution polymerization]

[0085] a polymerization reaction -- a batch method or a continuous magnetization method -- you may carry out by which approach. It faces carrying out a polymerization with a batch method, and the aforementioned catalyst component is used under the concentration explained below. the case where a vanadium system catalyst is used -- the concentration of the fusibility vanadium compound in a polymerization system -- usually -- 0.01 - 5 millimol / liter (polymerization volume) -- they are 0.05 - 3 millimol / liter preferably. A fusibility vanadium compound has the preferably 1 to 7 times more desirable thing of the concentration of the fusibility vanadium compound which exists in a polymerization system supplied by one 1 to 5 times the concentration of this still more preferably 10 or less times. Moreover, an organoaluminium compound is the mole ratio (aluminum/V) of an aluminum atom to the vanadium atom in a polymerization system, and is supplied in the amount of 3-20 preferably [it is desirable and] to 2-50, and a pan two or more.

[0086] A fusibility vanadium compound and an organoaluminium compound are usually diluted with said hydrocarbon solvent and/or liquefied monomer, and are supplied. Under the present circumstances, although it is desirable for the aforementioned concentration to dilute as for a fusibility vanadium compound, as for an organoaluminium compound, it is desirable to adjust to the concentration of 50 or less times [of the concentration in a polymerization system] arbitration, and to be supplied in a polymerization system.

[0087] moreover -- the case where a metallocene system catalyst is used -- the concentration of the metallocene compound in a polymerization system -- usually -- 0.00005 - 0.1 millimol / liter (polymerization volume) -- they are 0.0001 - 0.05 millimol / liter preferably. moreover, the mole ratio [as opposed to the transition metals in the metallocene compound in a polymerization system in an organic aluminium oxy compound] (aluminum/transition metals) of an aluminum atom -- it is -- 1-10000 -- it is preferably supplied in the amount of 10-5000.

[0088] the mole ratio [as opposed to the metallocene compound in a polymerization system in an ionization ionicity compound] (an ionization ionicity compound / metallocene compound) of an ionization ionicity compound -- expressing -- 0.5-20 -- it is preferably supplied in the amount of 1-10. Moreover, when an organoaluminium compound is used, it is usually used in about zero to 5 millimol / liter (polymerization volume), and an amount that serves as about zero to 2 millimol / liter preferably.

[0089] When carrying out a polymerization to the bottom of existence of said vanadium system catalyst, -50-+100 degrees C of -30-+80 degrees C of temperature are usually -20-+60 degrees C still more preferably preferably, and, as for a polymerization reaction, a pressure is preferably performed exceeding 0 exceeding 0 to the bottom of the condition below 2.0MPa(s) (20 kgf/cm², gage pressure) below 4.9MPa(s) (50 kgf/cm², gage pressure).

[0090] When carrying out a polymerization to the bottom of existence of said metallocene catalyst, -20-+180 degrees C of 0-170 degrees C of temperature are usually 80-170 degrees C still more preferably preferably, and, as for a polymerization reaction, a pressure is preferably performed exceeding 0

exceeding 0 to the bottom of the condition below 4.9MPa(s) (50 kgf/cm², gage pressure) below 7.8MPa (s) (80 kgf/cm², gage pressure).

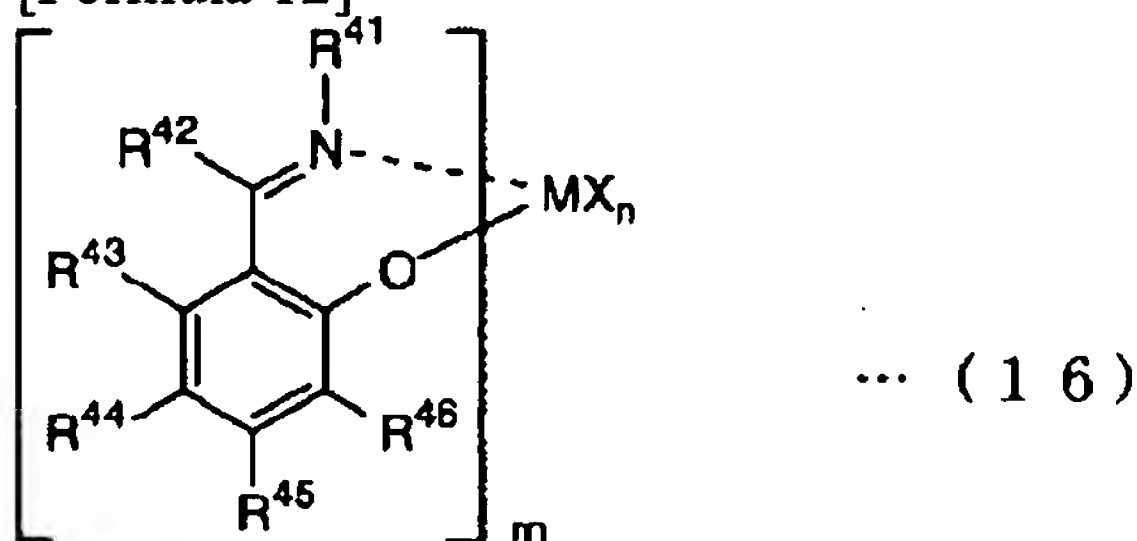
[0091] On the occasion of a polymerization, the alpha olefin used ethylene and if needed is supplied to a polymerization system at an amount rate from which the ethylene system polymer (A) of the above mentioned specific presentation is obtained. Moreover, molecular weight modifiers, such as hydrogen, can also be added on the occasion of a polymerization. Thus, if a polymerization is carried out, since the generated polymer will be obtained as polymerization liquid which usually contains this, if it processes with a conventional method, the ethylene system polymer (A) concerning this invention will be obtained.

[0092] As the synthetic approach of an ethylene system polymer (A), the method of using various complex compound catalysts in addition to the above-mentioned metallocene catalyst is mentioned, and the polymerization method using the complex compound given in JP,2001-2731,A as an example is mentioned. According to the catalyst for olefin polymerization which consists of at least one sort of compounds chosen from the compound which specifically reacts with the complex compound expressed with the following general formula (16), and the complex compound expressed with an organometallic compound, an organic aluminium oxy compound, and a general formula (16), and forms an ion pair, ethylene is homopolymerized or ethylene and an alpha olefin are copolymerized.

[0093] (Complex compound)

[0094]

[Formula 12]



[0095] (In addition, it is N [Although having configured is shown, M does not have to be made general even if it has configured in this invention.])

Among a general formula (16), M shows the transition-metals atom (a lanthanoids is also contained in three groups) of the 3-11th groups of a periodic table, is 3 - 9 group's (a lanthanoids is also contained in three groups) metal atom preferably, is the metal atom of 3 - 5 group and nine groups more preferably, is the metal atom of four groups or five groups still more preferably, and is titanium, a zirconium, and a hafnium especially preferably.

[0096] m -- 1-6 -- the integer of 1-4 is shown preferably. Even if R41-R46 are mutually the same, they may differ from each other, they may show a hydrogen atom, a halogen atom, a hydrocarbon group, heterocyclic compound residue, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, the Lynn content radical, a silicon content radical, a germanium content radical, or a tin content radical, may connect it mutually [two or more pieces] of these, and may form the ring.

[0097] In addition, as for R46, it is desirable that they are substituents other than hydrogen. R41-R46 may form the hydrocarbon ring in which 2 or more of radicals of these and the radical which adjoins preferably connect with mutually, and contains different atoms, such as a fat ring, a ring, or a nitrogen atom, and these rings may have the substituent further. Moreover, when m is two or more, R41-R46 belonging to one ligand, and R41-R46 belonging to other ligands may be connected. Furthermore, when m is two or more, even if R41 comrades, R42 comrades, R43 comrades, R44 comrades, R45 comrades, and R46 comrades are mutually the same, they may differ.

[0098] the number with which n fills the valence of M -- it is -- concrete -- 0-5 -- desirable -- 1-4 -- it is the integer of 1-3 more preferably. X shows a hydrogen atom, a halogen atom, a hydrocarbon group, an

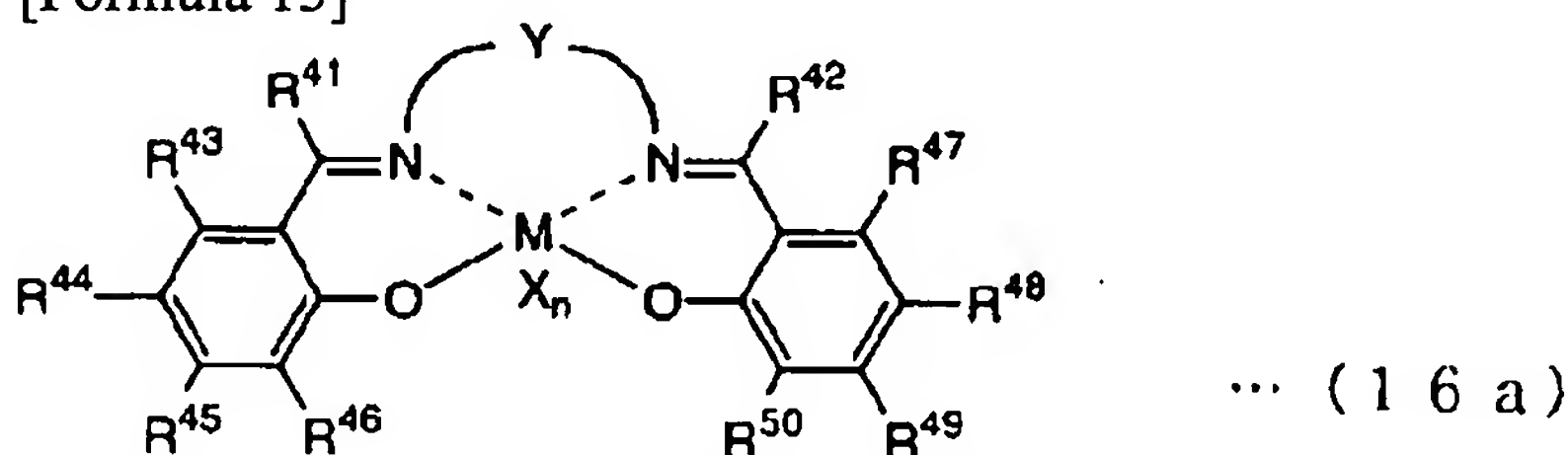
oxygen content radical, a sulfur content radical, a nitrogen content radical, a boron content radical, an aluminum content radical, the Lynn content radical, a halogen content radical, heterocyclic compound residue, a silicon content radical, a germanium content radical, or a tin content radical. In addition, when n is two or more, even if mutually the same, you may differ.

[0099] In addition, when n is two or more, it may join together mutually and two or more radicals which may differ even if two or more radicals shown by X are mutually the same, and are shown by X may form a ring. The concrete example of a complex compound expressed with such an above-mentioned general formula (16) is shown in paragraph number [of JP,2001-2731,A] [0065] - [0076].

[0100] Moreover, as a complex compound expressed with a general formula (16), there is a complex compound expressed with the following general formula (16a).

[0101]

[Formula 13]

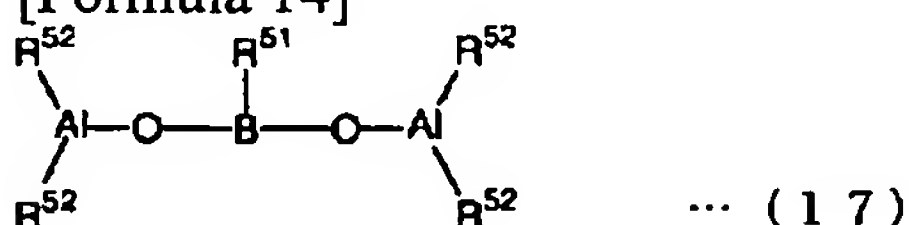


[0102] M shows the transition-metals atom of the 3-11th groups of a periodic table among a formula. R41-R50 You may differ, even if mutually the same. A hydrogen atom, a halogen atom, a hydrocarbon group, Heterocyclic compound residue, an oxygen content radical, a nitrogen content radical, a boron content radical, a sulfur content radical, The Lynn content radical, a silicon content radical, a germanium content radical, or a tin content radical is shown, it may connect mutually [two or more pieces] of these, and the ring may be formed. n It is the number which fills the valence of M. X A hydrogen atom, a halogen atom, a hydrocarbon group, An oxygen content radical, a sulfur content radical, a nitrogen content radical, a boron content radical, an aluminum content radical, The Lynn content radical, a halogen content radical, heterocyclic compound residue, a silicon content radical, a germanium content radical, or a tin content radical is shown, and when n is two or more It may join together mutually and two or more radicals which may differ even if two or more radicals shown by X are mutually the same, and are shown by X may form a ring. Y The divalent joint radical containing at least one sort of elements chosen from the group which consists of oxygen, sulfur, carbon, nitrogen, Lynn, silicon, a selenium, tin, and boron is shown, and when it is a hydrocarbon group, it is the radical which consists of three or more carbon numbers. When n is two or more, the ring which two or more X connects mutually and forms may be an aromatic series ring, or may be an aliphatic series ring.

[0103] The concrete example of a complex compound expressed with the above-mentioned general formula (16a) is shown in the paragraph number [0085] of JP,2001-2731,A thru/or [0087]. As an organometallic compound, the above-mentioned organoaluminium compound is used preferably. An organometallic compound is one-sort independent, or is combined two or more sorts and used. As an organic aluminium oxy compound, the above-mentioned organic aluminium oxy compound is used. Moreover, the organic aluminium oxy compound which contained the boron expressed with the following general formula (17) as an organic aluminium oxy compound can also be used.

[0104]

[Formula 14]



[0105] R51 shows the hydrocarbon group of the carbon atomic numbers 1-10 among a formula. You may differ, even if R52 is mutually the same, and a hydrogen atom, a halogen atom, and a carbon atomic number show the hydrocarbon group of 1-10. The above organic aluminium oxy compounds are one-

sort independent, or are combined two or more sorts and used.

[0106] The above-mentioned ionization ionicity compound is mentioned as a compound which reacts with the complex compound expressed with the above-mentioned general formula (16), and forms an ion pair. An ionization ionicity compound is one-sort independent, or is combined two or more sorts and used.

(Polymerization) A polymerization can be carried out also in any of liquid phase polymerization methods, such as a dissolution polymerization and a suspension polymerization, or a vapor-phase-polymerization method. As an inert hydrocarbon medium used in a liquid phase polymerization method, halogenated hydrocarbon or such mixture, such as aromatic hydrocarbon; ethylene chloride, such as alicycle group hydrocarbon; benzene, such as aliphatic hydrocarbon; cyclopentanes, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Deccan, a dodecane, and kerosene, a cyclohexane, and methylcyclopentane, toluene, and a xylene, chlorobenzene, and dichloromethane, etc. can be mentioned, and, specifically, the olefin itself can also be used as a solvent.

[0107] It faces performing the polymerization of an olefin using the above catalysts for olefin polymerization, and 10-12 to ten - two mols of complex compounds are usually used in an amount which becomes 10-10 to ten - three mols preferably. As for an organometallic compound, a mole ratio (an organometallic compound/M) with the transition-metals atom (M) of an organometallic compound and a complex compound is usually used in 0.01-100,000, and an amount that is preferably set to 0.05-50,000.

[0108] As for an organic aluminium oxy compound, the mole ratio (aluminum/M) of the aluminum atom in an organic aluminium oxy compound and the transition-metals atom in a complex compound (M) is usually used in 10-500,000, and an amount that is preferably set to 20-100,000. As for an ionization ionicity compound, a mole ratio (an ionization ionicity compound /M) with the transition-metals atom in an ionization ionicity compound and a complex compound (M) is usually used in 1-20, and an amount that is preferably set to 1-10.

[0109] Moreover, the range of -50-+200 degrees C of polymerization temperature of the olefin using such a catalyst for olefin polymerization is usually 0-170 degrees C preferably. the polymerization preassure force -- usually -- ordinary pressure - 9.8 MPa (100kg/cm², gage pressure), it is under the condition of ordinary pressure -4.9MPa (50kg/cm², gage pressure) preferably, and a polymerization reaction can be performed also in which approach of a batch process, half-continuous system, and continuous system. It is also possible to divide a polymerization into two or more steps where reaction conditions differ, and to perform it furthermore.

[0110] By this approach, the ethylene system polymer which includes the unsaturated bond of a vinyl mold or a vinylidene mold in the single-sided end of a polymer chain is obtained, and this ethylene system polymer is usable also as a grant object of -SO₃- of a denaturation ethylene system polymer (B). (B) A denaturation ethylene system polymer denaturation ethylene system polymer (B) is a denaturation ethylene system polymer to which ethylene homopolymerization, or ethylene / alpha olefin copolymer denaturalized with unsaturated carboxylic acid, its derivative, or sulfonate.

[0111] As ethylene homopolymerization, or the ethylene / alpha olefin copolymer (henceforth a "raw material ethylene system polymer") used for preparation of a denaturation ethylene system polymer (B), the above-mentioned ethylene system polymer (A) is mentioned, for example. A denaturation ethylene system polymer (B) can be conventionally prepared by the well-known approach. For example, (i) raw material ethylene system polymer, (ii) Carry out melting kneading under existence of polymerization initiators, such as organic peroxide (iii), or unsaturated carboxylic acid, its derivative, or sulfonate Or (i) ethylene system polymer, (ii) It is obtained by kneading unsaturated carboxylic acid, its derivative, or sulfonate under existence of polymerization initiators, such as organic peroxide (iii), in the solution which dissolved in the organic solvent.

[0112] As the unsaturated carboxylic acid used for the denaturation of a denaturation ethylene system polymer (B), or its derivative For example, a methyl acrylate, an ethyl acrylate, butyl acrylate, Acrylic-acid-sec-butyl, isobutyl acrylate, acrylic-acid propyl, Acrylic-acid isopropyl, acrylic-acid-2-octyl, acrylic-acid dodecyl, Acrylic-acid stearyl, acrylic-acid hexyl, acrylic-acid iso hexyl, Acrylic-acid

phenyl, acrylic-acid-2-chlorophenyl, an acrylic-acid diethylaminoethyl, Acrylic-acid-3-methoxy butyl, diethyleneglycol ethoxyl acrylate, Acrylic acid - Acrylic ester; methyl methacrylates, such as 2, 2, and 2-trifluoroethyl, Methacrylic acid ethyl, methacrylic-acid butyl, methacrylic-acid-sec-butyl, Methacrylic-acid isobutyl, methacrylic-acid propyl, methacrylic-acid isopropyl, Methacrylic-acid-2-octyl, methacrylic-acid dodecyl, stearyl methacrylate, Stearyl methacrylate, methacrylic-acid hexyl, methacrylic-acid DESHIRU, Methacrylic-acid phenyl, methacrylic-acid-2-chloro hexyl, diethylaminoethyl methacrylate, Methacrylic-acid-2-hexyl ethyl, methacrylic acid - Methacrylic ester: maleic-acid ethyl, such as 2, 2, and 2-trifluoroethyl, Maleic-acid propyl, maleic-acid butyl, a diethyl maleate, maleic-acid dipropyl, Maleates, such as dibutyl maleate : Fumaric-acid ethyl, fumaric-acid butyl, Fumaric-acid ester, such as fumaric-acid dibutyl; A maleic acid, boletic acid, Dicarboxylic acid, such as an itaconic acid, a crotonic acid, a NAJIKKU acid, and methyl hexahydrophthalic acid; anhydrides, such as a maleic anhydride, itaconic acid anhydride, an anhydrous citraconic acid, an anhydrous allyl compound succinic acid, anhydrous glutaconic acid, and an anhydrous NAJIKKU acid, etc. are mentioned.

[0113] As for a denaturation ethylene system polymer (B), it is desirable that the amount of denaturation in unsaturated carboxylic acid or its derivative is KOH titration conversion, and are per [30] 1g of polymers - 100mgKOH, and it is still more desirable that it is 30 - 60mgKOH. When the amount of denaturation in unsaturated carboxylic acid or its derivative is in above-mentioned within the limits, the hygroscopicity of the particle obtained from an aqueous dispersing element is moderate, and there is an inclination to excel in a water resisting property, weatherability, etc. Moreover, the phase inversion after water addition is enough, and there is an inclination for an aqueous dispersing element to be obtained by high yield.

[0114] When having denaturalized with sulfonate, it is desirable that the amount of denaturation is 0.1 to 100 millimol per 1g of polymers, and it is still more desirable that it is five to 50 millimol. When the amount of denaturation in sulfonate is in above-mentioned within the limits, there is an inclination which a non-emulsified object cannot generate easily and the aggregate of a sulfonate stops being able to generate easily other than an emulsification object.

[0115] The ethylene system polymer constituent aqueous dispersing element concerning preparation approach this invention of an ethylene system polymer constituent aqueous dispersing element can be prepared by making water distribute the ethylene system polymer constituent obtained from for example, the above-mentioned ethylene system polymer (A) and a denaturation ethylene system polymer (B). Specifically, melting kneading of an ethylene system polymer (A) and the denaturation ethylene system polymer (B) is carried out first. Under the present circumstances, as for the weight ratio (A/B) of an ethylene system polymer (A) and a denaturation ethylene system polymer (B), it is desirable that it is 95 / 5 - 50/50, and it is still more desirable that it is 90 / 10 - 60/40.

[0116] Although the temperature in the case of melting kneading is high among an ethylene system polymer (A) and a denaturation ethylene system polymer (B), it is beyond temperature from which melt viscosity is preferably set to 105 or less poises more than the melting point of the direction. Next, phase inversion of the fused resin can be carried out to an aqueous dispersing element by adding water in a melting kneading object, and kneading resin and water, while resin has been in a melting condition so that resin solid content may serve as a particulate material. An alkali and a surfactant which are later mentioned at this process can be added.

[0117] As for water, it is desirable to add preferably one to 40% of the weight to the whole ethylene system polymer constituent aqueous dispersing element in an amount which becomes 15 - 30 % of the weight. Although it can add as it is or can add as a water solution, as for an alkali, dissolving and using for the above-mentioned water is desirable. The addition of an alkali is a complement usually neutralizing a denaturation ethylene system polymer.

[0118] As for 50% mean particle diameter of volume of the particulate material of an ethylene system polymer constituent aqueous dispersing element, it is desirable that it is 0.1-10 micrometers, and it is still more desirable that it is 0.2-5 micrometers. Thus, solid content is 60 % of the weight or more, and, as for the obtained ethylene system polymer constituent aqueous dispersing element, it is desirable that

it is 70 % of the weight or more. Such an ethylene system polymer constituent aqueous dispersing element of high solid content is a solid-state seemingly, and it is desirable by adding water that it is what solid content distributes to homogeneity in the aqueous phase as a very fine particle.

[0119] Although the ethylene system polymer constituent aqueous dispersing element concerning this invention can be used for various applications, it can be suitably used as the additive for printing ink, especially an additive for water color ink, and can give the engine performance having abrasion resistance and blocking resistance excellent in ink. The ethylene system polymer constituent aqueous dispersing element of high solid content turns into a liquefied aqueous dispersing element with a fluidity by adding and (warm water ****) stirring water or a basic water solution if needed. Thus, by carrying out detailed distribution of the ethylene system polymer constituent aqueous dispersing element of high solid content underwater further at homogeneity, it becomes possible to adjust broadly liquid nature, such as solid content concentration, viscosity, and pH, and the addition to wide range ink is attained. Thus, the engine performance prepared ethylene system polymer constituent aqueous dispersing elements, such as solid content concentration, viscosity, and pH, also had the engine performance, and abrasion resistance and blocking resistance excellent in ink can be given.

[0120] The following matter which acts as a base underwater as an alkali, for example, the oxide of alkali-metal; alkaline-earth-metal; ammonia; amine; alkali metal, a hydroxide, a weak acid salt or the oxide of hydride; alkaline earth metal, a hydroxide, a weak acid salt, or a hydride; (Alkali) The alkoxide of alkali metal or alkaline earth metal etc. is mentioned. As an alkali metal, sodium, a potassium, etc. are still more specifically mentioned. Calcium, strontium, barium, etc. are mentioned as an alkaline earth metal. As an amine, inorganic amines, such as a hydroxylamine and a hydrazine, Monomethylamine, ethylamine, ethanolamine, cyclohexylamine, etc. are mentioned. As the oxide of alkali metal or alkaline earth metal, a hydroxide, a weak acid salt, or a hydride, sodium oxide, A sodium peroxide, an oxidization potassium, potassium peroxide, a strontium oxide, The barium oxide, a sodium hydroxide, a potassium hydroxide, a calcium hydroxide, A strontium hydroxide, a barium hydroxide, sodium hydride, potassium hydride, Calcium hydride, a sodium carbonate, potassium carbonate, a sodium hydrogencarbonate, A potassium hydrogencarbonate, calcium hydrogencarbonate, sodium acetate, potassium acetate, Calcium acetate etc. is mentioned and the fourth class ammonium compounds, such as ammonium hydroxide and tetramethylammonium hydroxide, a hydrazine hydrate, etc. are mentioned as a compound of ammonia and an amine.

[0121] (Surface active agent) In the ethylene system polymer constituent aqueous dispersing element concerning this invention, a surface active agent is used together if needed. When a denaturation ethylene polymer (B) denaturalizes with a carboxylic acid or its derivative, the Nonion system surface active agent is suitable, and when a denaturation ethylene system polymer (B) denaturalizes with sulfonic acid, an anionic surface active agent is suitable. It can raise water-dispersion [of an ethylene system polymer constituent] by using a surface active agent.

[0122] what has hydrophile-lipophile balance (HLB) low as a nonionic surface active agent -- the thing of the range of 5-10 is especially used for HLB preferably ten or less still more preferably 12 or less. Specifically, the surfactant which has HLB in above-mentioned within the limits is used among polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene fatty acid ester, the polyoxyethylene-fatty-acid-amide ether, polyhydric-alcohol fatty acid ester, polyoxyethylene polyhydric-alcohol fatty acid ester, fatty-acid cane-sugar ester, an ARUKI roll amide, a polyoxyalkylene block copolymer, etc. In these nonionic surface active agents, generally, since HLB will fall if the content of a polyoxyethylene unit decreases, the nonionic surface active agent of desired HLB is obtained by adjusting the number of addition mols of ethyleneoxide. The addition pile of the Nonion system surface active agent has 0.3 - 2.0% of the weight of the preferably desirable range 0.1 to 10% of the weight per denaturation ethylene system polymer.

[0123] As an anion system surfactant, for example The 1st class higher-fatty-acid salt, the 2nd class higher-fatty-acid salt, The 1st class fatty alcohol sulfate, the 2nd class fatty alcohol sulfate, High-class alkyl disulfon acid chloride, a sulfonic-acid-ized higher-fatty-acid salt, a higher-fatty-acid sulfate salt, A higher-fatty-acid ester sulfonate, the sulfate salt of the higher-alcohol ether, The sulfonate of the higher-

alcohol ether, the ARUKI roll-ized sulfate salt of a higher-fatty-acid amide, If it reacted with alkalis, such as alkylbenzene sulfonates, an alkylphenol sulfonate, an alkyl naphthalenesulfonic acid salt, and an alkyl benzimidazole sulfonate, and became an anionic surface active agent, what kind of thing may be used. The more concrete compound name of these surfactants is shown for example, in the Horiguchi **** "a synthetic surfactant" (Showa 41 Sankyo Publishing). Also in these, especially alkylbenzene sulfonates are suitable and more specifically sodium dodecylbenzenesulfonate.

[0124] As an approach of making such a surface active agent containing, you may blend as a raw material with an ethylene system polymer (A) and a denaturation ethylene system polymer (B), it considers as the water solution beforehand, and you may add at the time of melting kneading. Moreover, as a content, 10 or less % of the weight is desirable to an ethylene system polymer constituent aquosity dispersing element, and 3 or less % of the weight is still more desirable. When a surfactant is contained in the amount exceeding 10 % of the weight, the hygroscopicity of the particle obtained from an aquosity dispersing element may be high, and a water resisting property, weatherability, etc. may fall.

[0125] As for the ethylene system polymer constituent organic solvent dispersing element concerning ethylene system polymer constituent organic solvent dispersing element this invention, a hydrocarbon solvent comes to distribute the particle of the above-mentioned ethylene system polymer constituent. Such an ethylene system polymer constituent organic solvent dispersing element can be prepared by re-distributing the particle which removes water and is obtained for example, from the above-mentioned ethylene system polymer constituent aquosity dispersing element to a hydrocarbon solvent.

[0126] The particle of the ethylene system polymer constituent currently distributed is made to condense by adding the acid of a complement specifically neutralizing the alkali first used for preparation of the above-mentioned ethylene system polymer constituent aquosity dispersing element. If an acid is added to an aquosity dispersing element, the base used as the counter ion of a carboxyl anion will be neutralized by the acid, and a carboxyl group will serve as a hydrogen ion mold with small ionization degree. For this reason, underwater self-emulsifiability or self-dispersibility decreases sharply and condenses the particle of an ethylene system polymer constituent.

[0127] As an acid used for neutralization, organic acids, such as inorganic acids, such as a sulfuric acid, a hydrochloric acid, a nitric acid, and a phosphoric acid, or various sulfonic acid, are used, for example. When such an acid is used, the salt formed as a result of neutralization shows water solubility. As for the acid used for neutralization, pH of the aqueous phase is usually used six or less in an amount which is preferably set to 2-4. The temperature of the aquosity dispersing element at the time of neutralization is usually room temperature extent, and may be warmed to about 60 degrees C by request. Moreover, the concentration of aquosity dispersion liquid has 5 - 50% of the weight of the desirable range, when operability is taken into consideration.

[0128] Next, the particle and water of an ethylene system polymer constituent which were condensed in this way are separated. Although especially the separation approach is not limited, approaches, such as filter filtration, centrifugal separation, and floatation, are used, for example. In addition, if the centrifugal separator equipped with the filter is used, the same equipment can perform efficiently removal actuation of water and washing actuation by the hydrophilic solvent of a wet cake which is mentioned later.

[0129] Before drying the wet cake of the aggregate obtained by separating the particle and water of an ethylene system polymer constituent, a hydrophilic solvent permutes and removes the moisture which remains in a wet cake by washing with a hydrophilic solvent. Thus, most moisture which remains is removable by washing a wet cake with a hydrophilic solvent. And depending on washing with a hydrophilic solvent in this way, a wet cake will not be in dryness. Therefore, redispersible [of a particle / as opposed to an organic solvent in the particle of an ethylene system polymer constituent] does not fall, without spoiling oleophilic [which the ethylene system polymer constituent originally has].

[0130] As a hydrophilic solvent, the solvent which dissolves 10% of the weight or more in ordinary temperature respectively is used for both of the hydrocarbon system organic solvent used as water and a re-dispersion medium here. As such a hydrophilic solvent, alcohols, ketones, and ether are used

preferably. In addition, when the hydrocarbon solvent used for the re-distribution mentioned later is a hydrophilic solvent, the hydrocarbon solvent used for re-distribution can also be used for washing of the above-mentioned wet cake. A hydrophilic solvent is used in the particle in a wet cake, this weight, or the amount beyond it.

[0131] Then, the wet cake washed with the hydrophilic solvent is re-distributed in a hydrocarbon solvent. As a hydrocarbon solvent, although the hydrocarbon of arbitration can be used, when using an ethylene system polymer constituent organic solvent dispersing element, for example as compounding agents, such as rotogravure ink, toluene, a xylene, methyl isobutyl ketone, isopropyl alcohol, etc. are desirable, and when using as compounding agents, such as offset ink, it is more desirable than the above-mentioned solvent to use the fractional distillation solvent of n-Deccan of a high-boiling point, gas oil, or gas oil etc.

[0132] What is necessary is just to usually agitate for [10 minutes -] 300 minutes using churning equipment, in order to make a hydrocarbon solvent re-distribute the particle of an ethylene system polymer constituent. By using high performance distribution equipment like especially a homomixer, re-distribution can be performed more efficiently. Thus, the dispersing element (ethylene system polymer constituent organic solvent dispersing element) which the particle of an ethylene system polymer constituent distributed in the hydrocarbon solvent is obtained by making a hydrocarbon solvent re-distribute a wet cake. Thus, in the obtained ethylene system polymer constituent organic solvent dispersing element, moisture content is 0 - 1.0% of the weight of the range especially preferably 2 or less % of the weight preferably 2.5 or less % of the weight.

[0133] In order to raise that storage stability, the dispersant or viscosity controlling agent like an oil solubility giant-molecule polymer or organic bentonite may be blended with this ethylene system polymer constituent organic medium dispersing element. engine-performance ***** which had especially the abrasion resistance and blocking resistance which could use suitably as an additive for printing ink, and were excellent in ink although such an ethylene system polymer constituent organic medium dispersing element could be used for various applications -- things are made.

[0134] moreover, engine-performance ***** having the abrasion resistance and blocking resistance which the wet cake which washed the wet cake of the aggregate obtained by separating the particle and water of the above-mentioned ethylene system polymer constituent and this wet cake with the hydrophilic solvent could also be suitably used especially as an additive for printing ink, and excelled [cake] in ink -- things are made.

Solid content blends preferably the additive for printing ink concerning additive this invention for ink 0.1 to 10% of the weight to the whole quantity of printing ink in an amount which becomes 0.5 - 5 % of the weight.

[0135] When the amount of the solid content originating in the additive for printing ink in printing ink is in above-mentioned within the limits, printing ink tends to be excellent in the balance of abrasion resistance and BUROKINGU-proof nature. As the addition approach of the additive for printing ink, it can add at any process in the conventional printing ink production process. That is, the additive for printing ink may be mixed and ink-ized to what could ink-ize what performed distribution and kneading for both the pigment and the additive for printing ink on the varnish, and passed through distribution and a kneading process.

[0136] Although the melting kneading means which can be used for the process of this invention may use what kind of well-known approach, a twin screw extruder, a 1 shaft extruder, a kneader, and an alder BARI mixer can be illustrated suitably. Moreover, at the time of preparation of printing ink, the various subsidiary materials which can usually be used for printing ink, for example, a dispersant, an emulsifier, a surfactant, a stabilizing agent, a wetting agent, a thickener, a frothing agent, a defoaming agent, a coagulant, a gelling agent, a sedimentation inhibitor, an electrification control agent, an antistatic agent, an antioxidant, a softener, a plasticizer, a bulking agent, a coloring agent, oderant, a antitack agent, a chicken type agent, etc. may be used together in the range which do spoil the engine performance with the additive for printing ink

[0137] Although not limited especially about the resin used as the principal component of printing ink,

usually Starch, a dextrin, alginate, cellulose ester, cellulose ether, Polyvinyl alcohol, polyvinyl methyl ether, polyacrylamide, Water soluble resin, such as polyethylene oxide and polyacrylate, a shellac, A styrene-ized shellac, styrene maleic resin, rosin maleic resin, Colloidal dispersions, such as casein and its derivative, and an acrylic copolymer, Emulsions, such as acrylic resin, acrylic styrene copolymerization resin, vinyl acetate system resin, styrene resin, vinyl chloride system resin, synthetic rubber latex, polyurethane, polyester, alkyd resin, EPO pheasant ester, and rosin ester, are used.

[0138]

[Effect of the Invention] The ethylene system polymer constituent aqueosity dispersing element, the ethylene system polymer constituent organic solvent dispersing element, and the additive for printing ink concerning this invention can give the engine performance having abrasion resistance and blocking resistance excellent in ink.

[0139]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these examples. The measuring method of various kinds of characteristic values was performed by the following approaches.

1. It investigated by making the wire gauze of 100 meshes of distributed conditions of an aqueosity dispersing element pass dispersion liquid.

2. Particle Size of Aqueosity Dispersing Element (Micrometer)

By micro truck HRA (micro truck company make), 50% mean particle diameter of volume was measured.

3. It measured in the PHPH meter (product made from HORIBA) of an aqueosity dispersing element.

4. Base Material Which Prints Abrasion Resistance Evaluation Water Color Ink of Water Color Ink : K Liner Paper (Oji Paper Co., Ltd. Make)

White liner paper (Settsu Corp. make)

Water color ink: What mixed and prepared an aqueosity varnish (Joncryl 62: Johnson polymer), pigment dispersion liquid (WS RED R-1: TOYO INK MFG.), and a binder (Joncryl 450) at a rate of 20:40:40.

[0140] The evaluation approach made from wear-proof: Leave and dry for two days at ** room temperature which carries out coating of the ink so that it may become the ** above-mentioned base material with 3-4 micrometers of desiccation thickness.

** Gakushin-type antifriction testing-machine II mold (Circuit tester Industry) use friction paper: -- a CRC board load and count of friction: -- grind against the board which attached the 200gx 500 times ** evaluation ink coating side in the friction child, and perform five-step evaluation by the degree which ink imprinted on the board.

(Good) 5-4-3-2-1 (wrong)

The blocking-resistance evaluation approach: Pile up two sheets inside, face across the coating side of the ink coated paper after desiccation of ** above with a glass plate, and carry weight so that it may become load 10 g/cm² on a smooth base. this -- constant temperature -- constant temperature (25 degrees C, 50%) -- five steps of situations when pulling apart two sheets of papers are evaluated inside and after 24-hour neglect.

[0141] Situation of a printing side (good) 5-4-3-2-1 (wrong)

[0142]

[The example 1 of manufacture] manufacture of an ethylene system polymer -- the autoclave made from stainless steel of 2l. of content volume which fully carried out the nitrogen purge -- hexane 950ml and propene 50ml was inserted in, and hydrogen was introduced until it became 1.0kg/cm² (gage pressure). Subsequently, triisobutylaluminum after carrying out the temperature up of the temperature in a system to 150 degrees C 0.3 millimol, triphenylcarbenium tetrakis (PENDA fluoro phenyl) borate The polymerization was started by pressing 0.004 millimol and dimethyl (t-butyl amide) (tetramethyl-eta⁵-cyclopentadienyl) silane titanium JIKURO light (sigma alto rich company make) 0.02 millimol fit with ethylene. Then, by supplying only ethylene continuously, total pressure was kept at 30kg/cm² (gage pressure), and the polymerization was performed for 20 minutes at 150 degrees C. After suspending a polymerization by adding a small amount of ethanol in a system, unreacted ethylene and an unreacted

propene were purged. The obtained polymer solution was dried under 100-degree-C reduced pressure overnight.

[0143] Consequently, 32.5g of ethylene propene copolymers whose propene content Mn is 2,050 and is 7.3-mol %, whose consistencies are 920 kg/m³ and whose crystallization temperature is 93 degrees C was obtained (this copolymer was set to "WAX-1").

[0144]

[The example 2 of manufacture] It sets to the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, and is a hexane. 65ml was inserted in by having made 935ml and an alpha olefin component into 1-butene, and the polymerization was performed like the example 1 of manufacture except having introduced hydrogen until it became 1.5kg/cm² (gage pressure).

[0145] Consequently, ethylene and 37.5g of 1-butene copolymers whose 1-butene content Mn is 1,900 and is 5.6-mol %, whose consistencies are 920 kg/m³ and whose crystallization temperature is 93 degrees C were obtained (this copolymer was set to "WAX2").

[0146]

[The example 3 of manufacture] It sets to the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, and is a hexane. 80ml was inserted in by having made 920ml and an alpha olefin component into 1-hexene, and the polymerization was performed like the example 1 of manufacture except having introduced hydrogen until it became 2.0kg/cm² (gage pressure).

[0147] Consequently, ethylene and 43.2g of 1-hexene copolymers whose 1-hexene content Mn is 2,100 and is 3.4-mol %, whose consistencies are 917 kg/m³ and whose crystallization temperature is 93 degrees C were obtained (this copolymer was set to "WAX3").

[0148]

[The example 4 of manufacture] It sets to the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, and is a hexane. It inserted in one time 90m by having made 910ml and an alpha olefin component into 4-methyl-1-pentene, and the polymerization was performed like the example 1 of manufacture except having introduced hydrogen until it became 2.0kg/cm² (gage pressure).

[0149] Consequently, ethylene and 41.2g of 4-methyl-1-pentene copolymers whose 4-methyl-1-pentene content Mn is 2,000 and is 3.7-mol %, whose consistencies are 918 kg/m³ and whose crystallization temperature is 93 degrees C were obtained (this copolymer was set to "WAX4").

[0150]

[The example 5 of manufacture] It sets to the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, and is a hexane. 65ml was inserted in by having made 935ml and an alpha olefin component into 1-butene, and the polymerization was performed like the example 1 of manufacture except having introduced hydrogen until it became 3.5kg/cm² (gage pressure).

[0151] Consequently, ethylene and 31.2g of 1-butene copolymers whose 1-butene content Mn is 600 and is 5.2-mol %, whose consistencies are 920kg/m³ and whose crystallization temperature is 92 in ** were obtained (this copolymer was set to "WAX5").

[0152]

[The example 6 of manufacture] It sets to the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, and is a hexane. 65ml was inserted in by having made 935ml and an alpha olefin component into 1-butene, and the polymerization was performed like the example 1 of manufacture except having introduced hydrogen until it became 1.0kg/cm² (gage pressure).

[0153] Consequently, ethylene and 38.8g of 1-butene copolymers whose 1-butene content Mn is 4,000 and is 5.7-mol %, whose consistencies are 920 kg/m³ and whose crystallization temperature is 92 degrees C were obtained (this copolymer was set to "WAX6").

[0154]

[The example 7 of manufacture] It is a hexane, without using a propene in the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer. The polymerization was performed like the example 1 of manufacture except having introduced 935ml and hydrogen until it became 1.0kg/cm² (gage pressure).

[0155] Consequently, ethylene polymer whose Mn is 2,000, whose consistencies are 977 kg/m³ and whose crystallization temperature is 110 degrees C 38.8g was obtained (this copolymer was set to "WAX7").

[0156]

[The example 1 of comparison manufacture] Within the glass autoclave of 1.5l. of preparation content volume of a catalyst, it is commercial anhydrous salt-ized magnesium. It is a hexane about 25g. It was made to suspend in 500ml. It is ethanol, keeping this at 30 degrees C and agitating it. 92ml was dropped in 1 hour and it was made to react for further 1 hour. After reaction termination, diethyl aluminum mono-chloride 93ml was dropped in 1 hour and it was made to react for further 1 hour. After reaction termination, titanium tetrachloride 90ml is dropped, the temperature up of the reaction container was carried out to 80 degrees C, and it was made to react for 1 hour.

[0157] After reaction termination, the solid-state section was washed by the hexane until the titanium of isolation was no longer detected by the decantation. The quantum of the titanium concentration was carried out with titration by having made this thing into hexane suspension, and the following experiments were presented.

manufacture of an ethylene system polymer -- the autoclave made from stainless steel of 2l. of content volume which fully carried out the nitrogen purge -- hexane 930ml and 1-butene 1 was inserted in 70m, and hydrogen was introduced until it became 20.0kg/cm² (gage pressure). Subsequently, after carrying out the temperature up of the temperature in a system to 170 degrees C, the polymerization was started by pressing 0.008 millimols fit with ethylene by the titanium component atom conversion obtained with triethylaluminum 0.1 millimol, ethylaluminium sesquichloride 0.4 millimol, and the above. Then, by supplying only ethylene continuously, total pressure was kept at 40kg/cm² (gage pressure), and the polymerization was performed for 40 minutes at 170 degrees C.

[0158] After suspending a polymerization by adding a small amount of ethanol in a system, unreacted ethylene and 1-butene were purged. The obtained polymer solution was dried under 100-degree-C reduced pressure overnight. Consequently, the ethylene and 1-butene copolymer whose 1-butene content Mn is 2,000 and is 5.4-mol %, whose consistencies are 917 kg/m³ and whose crystallization temperature is 101 degrees C 129g was obtained (this copolymer was set to "WAX8").

[0159]

[The example 2 of comparison manufacture] In the polymerization of the example 1 of manufacture comparison manufacture of an ethylene system polymer, 150ml was inserted in by having made hexane 850ml and an alpha olefin component into 4-methyl-1-pentene, and the polymerization was performed like the example 1 of comparison manufacture except having introduced hydrogen until it became 21.0kg/cm² (gage pressure).

[0160] Consequently, ethylene and 99g of 4-methyl-1-pentene copolymers whose 4-methyl-1-pentene content Mn is 2,100 and is 3.7-mol %, whose consistencies are 919 kg/m³ and whose crystallization temperature is 105 degrees C were obtained (this copolymer was set to "WAX9").

[0161]

[The example 3 of comparison manufacture] A propene is not used in the polymerization of the example 1 of manufacture manufacture of an ethylene system polymer, but it is a hexane. The polymerization was performed like the example 1 of manufacture except having introduced 1000ml and hydrogen until it became 2.5kg/cm² (gage pressure).

[0162] Consequently, ethylene polymer whose Mn is 2,000, whose consistencies are 977 kg/m³ and whose crystallization temperature is 126 degrees C 34.4g was obtained (this copolymer was set to "WAX10").

[0163]

[The example 4 of comparison manufacture] the polymerization of the example 1 of manufacture

manufacture of an ethylene system polymer -- setting -- hexane 920ml and propene 80ml -- the polymerization was performed like the example 1 of manufacture except having inserted in. Consequently, ethylene propene copolymer whose propene content Mn is 1,800 and is 11.2-mol %, whose consistencies are 897kg/m³ and whose crystallization temperature is 81 degrees C 29.9g was obtained (this copolymer was set to "WAX11").

[0164]

[Table 1]

表 1

	α -オレフィン 種	α -オレフィン 含有量 (mol%)	数平均 分子量 (Mn)	密度 (D) (g/cm ³)	式 (I) の左辺	結晶化 温度 (Tc) (°C)	
WAX1	プロペン	7.3	2050	920	94.9	93	製造例 1
WAX2	1-ブテン	5.6	1900	920	94.9	93	製造例 2
WAX3	1-ヘキセン	3.4	2100	917	93.5	93	製造例 3
WAX4	4-メチル-1- ペンテン	3.7	2000	918	93.9	93	製造例 4
WAX5	1-ブテン	5.2	600	920	94.9	92	製造例 5
WAX6	1-ブテン	5.7	4000	920	94.9	92	製造例 6
WAX7	無し	0	2000	977	123	110	製造例 7
WAX8	1-ブテン	5.4	2000	917	93.5	101	製造 比較例 1
WAX9	4-メチル-1- ペンテン	3.7	2100	919	94.4	105	製造 比較例 2
WAX10	無し	0	2000	977	124.9	126	製造 比較例 3
WAX11	プロペン	11.2	1800	897	83.4	81	製造 比較例 4

[0165]

[The example 8 of manufacture] The manufacture molecular weight of a denaturation ethylene system polymer is 2,200, and consistencies are 0.92 g/cm³. Straight chain-like polyethylene wax whose melt viscosity it has 0.5 internal duplex association per 1,000 carbon atom, and is 60cP(s) (160 degrees C) 150g It put into the 300 cc glass container equipped with the impeller, and after heating and carrying out melting with an oil bath, nitrogen gas was blown by the rate of flow of about 40l. / hr from the glass container pars basilaris ossis occipitalis at 150 degrees C for 30 minutes, and the nitrogen purge of the inside of a container was carried out. Next, maleic anhydride of a melting condition 25g, benzoyl peroxide After 5g was dropped over 2 hours, it was made to react at 150 degrees C for 1 hour. After decompressing the bottom of churning, and the inside of a container to 5mmHg(s), maintaining after reaction termination for 1 hour and removing volatile components, such as an unreacted maleic anhydride and a benzoyl peroxide decomposition product, the generated maleic-anhydride content polyethylene was picked out from the container.

[0166] Consequently, the maleic-anhydride denaturation polyethylene whose acid number is the 60 mgKOH/g-denaturation wax, whose intrinsic viscosity [η] is 0.17 dl/g and whose melting point is 110 degrees C was obtained (this denaturation polymer was considered as "denaturation WAX1").

[0167]

[The example 9 of manufacture] The 500ml round bottom flask equipped with the nitrogen purge, the capacitor, the air agitator, and the thermometer for the hexane (polyethylene oligomer (Mw/Mn:1.9 [η]:0.11 dl/g, Mn:900] number of vinyl groups per 1,000 carbon: 14.6 pieces) 10g and 100ml) manufactured by the approach of a publication for the synthetic example 1 of manufacture JP,2001-

2731,A of a denaturation ethylene system polymer was loaded. This loading object was stirred, it heated at 53 degrees C, and the polymer was dissolved. Subsequently the 2ml sulfuric acid was added for the 5.1ml acetic anhydride after cooling at 35 degrees C. This reaction mixture was stirred, it kept at 35 degrees C, and the acetic anhydride of a 2.5ml addition and the sulfuric acid of a 1ml addition were added after 15 minutes. Stirring this reaction mixture was continued at 35 degrees C for a total of 1 hour. Then, the 1ml methanol was added to the 4ml methanol which dissolved in 2ml water and 0.42g NaOH, and a list. Subsequently, overnight neglect was carried out, steam stripping was carried out continuously, overnight desiccation was carried out in the hood, vacuum furnace desiccation was carried out at 60 degrees C, and this reaction mixture was made into fixed weight. The sulfonation agent (and neutralizer) used in this example presupposed substantially that it is superfluous, in order to secure perfect sulfonation.

[0168] Consequently, the sulfonic acid denaturation polyethylene whose amount of denaturation is a 1 mmol/g-denaturation wax, whose intrinsic viscosity $[\eta]$ is 0.12 dl/g and whose melting point is 120 degrees C was obtained (this denaturation polymer was considered as "denaturation WAX2").

[0169]

[Table 2]

表 2

	変性種	変性量	$[\eta]$ (dl/g)	融点 (℃)	
変性 WAX1	無水マレイン酸	酸価=60mgKOH/g	0.17	110	製造例 8
変性 WAX2	-SO ₃ -	1mmol/g-変性ワックス	0.12	120	製造例 9

[0170]

[The synthetic example 1] WAX1 [140g] was put into the 1l. autoclave equipped with the impeller, and carried out melting mixing for 60g and denaturation WAX1 at 140 degrees C at it. After mixing, heating was continued for further 1 hour, nitrogen was blown into coincidence by the rate of flow of 10l. / hr, bubbling was performed, and melting mixture was obtained. The 150-degree C volatile matter of the obtained melting mixture was 0.12%.

[0171] Next, it is water to the proof-pressure homomixer of 4l. of inner capacity. 1500ml and potassium hydroxide 8.4g was put in, and the melting mixture obtained above was supplied over 1 hour with the gear pump, having heated at 140 degrees C and agitating by 5000rpm. Then, for 15 more minutes, after churning, it cooled to the room temperature and aqueosity dispersion liquid were obtained. The particulate material in the obtained aqueosity dispersion liquid was a real ball-like, and when it measured mean particle diameter, it was 0.6 micrometers. Even if it put these aqueosity dispersion liquid for one week, separation did not take place.

[0172]

[The synthetic examples 2-8] Aqueosity dispersion liquid were obtained by the same approach as the synthetic example 1 except WAX and Denaturation WAX having been shown in Table 3. The description of the obtained aqueosity dispersion liquid was described in Table 3.

[0173]

[The examples 1-5 of comparison composition] Aqueosity dispersion liquid were obtained by the same approach as the synthetic example 1 except having considered as the value which should show WAX and Denaturation WAX in Table 3, and showed the rotational frequency of a proof-pressure homomixer in Table 3. The description of the obtained aqueosity dispersion liquid was described in Table 3.

[0174]

[Table 3]

表 3

		合 成 例								比 較 合 成 例				
		1	2	3	4	5	6	7	8	1	2	3	4	5
エチレン系 重合体（g）	WAX1	60	60	—	—	—	—	—	—	—	—	—	—	—
	WAX2	—	—	60	—	—	—	—	—	—	—	—	—	—
	WAX3	—	—	—	60	—	—	—	—	—	—	—	—	—
	WAX4	—	—	—	—	60	—	—	—	—	—	—	—	—
	WAX5	—	—	—	—	—	60	—	—	—	—	—	—	—
	WAX6	—	—	—	—	—	—	60	—	—	—	—	—	—
	WAX7	—	—	—	—	—	—	—	60	—	—	—	—	—
	WAX8	—	—	—	—	—	—	—	—	60	—	—	—	—
	WAX9	—	—	—	—	—	—	—	—	—	60	—	—	—
	WAX10	—	—	—	—	—	—	—	—	—	—	60	—	—
	WAX11	—	—	—	—	—	—	—	—	—	—	—	60	60
変性ワックス系 重合体（g）	変性WAX1	140	—	140	140	140	140	140	140	140	140	140	140	140
	変性WAX2	—	140	—	—	—	—	—	—	—	—	—	—	—
耐圧ミキサの回転数 （rpm）		5000	5000	5000	5000	5000	5000	5000	5000	4000	4000	5000	5000	5000
水添加量 （ml）		1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500
水酸化カリウム （g）		8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
水性分散体の 体積平均粒径 （μm）		0.6	0.4	0.6	0.6	0.3	3.1	0.7	0.6	35	40	0.6	0.3	0.3

[0175]

[Example 1] The aqueous dispersing element compounded in the synthetic example 1 was added and stirred 1% by the solid content ratio of concentration to the aforementioned water color ink, and was made into the sample. After carrying out coating of this to K liner according to the aforementioned abrasion resistance evaluation approach and drying between two days of room temperatures, the abrasion resistance was evaluated. The result was described in Table 4.

[0176]

[Example 2] Except having changed desiccation conditions in 120 degrees C and 20 minutes, the same evaluation as an example 1 was performed, and abrasion resistance was evaluated. The result was described in Table 4.

[0177]

[Examples 3-11] Except having changed, as the aqueous dispersing element and base material to be

used were described in Table 4, the same evaluation as an example 1 was performed, and abrasion resistance was evaluated. The result was described in Table 4.

[0178]

[The examples 1-6 of a comparison] Except having changed, as the aquosity dispersing element and base material to be used were described in Table 4, the same evaluation as an example 1 was performed, and abrasion resistance was evaluated. The result was described in Table 4.

[0179]

[Table 4]

表 4

	水性分散体	粒径 (μm)	基材	乾燥条件	耐摩耗性	耐ブロッキング 性
実施例 1	合成例 1	0.6	K ライフ-	室温	4~5	5
実施例 2	合成例 1	0.6	K ライフ-	120℃	4~5	5
実施例 3	合成例 1	0.6	白ライフ-	室温	4~5	5
実施例 4	合成例 1	0.6	白ライフ-	120℃	4~5	5
実施例 5	合成例 2	0.4	K ライフ-	室温	4~5	5
実施例 6	合成例 3	0.6	K ライフ-	室温	4~5	5
実施例 7	合成例 4	0.6	K ライフ-	室温	4~5	5
実施例 8	合成例 5	0.3	K ライフ-	室温	4~5	5
実施例 9	合成例 6	3.1	K ライフ-	室温	4~5	5
実施例 10	合成例 7	0.7	K ライフ-	室温	5	5
実施例 11	合成例 8	0.6	K ライフ-	室温	4~5	5
比較例 1	比較合成例 1	35	K ライフ-	室温	1	2
比較例 2	比較合成例 2	40	K ライフ-	室温	1	2
比較例 3	比較合成例 3	0.6	K ライフ-	室温	4	4
比較例 4	比較合成例 3	0.6	K ライフ-	120℃	4	4
比較例 5	比較合成例 4	0.3	K ライフ-	室温	3	4
比較例 6	比較合成例 5	0.3	K ライフ-	室温	4	2

[0180]

[The synthetic example 9] The aquosity dispersion liquid obtained in the example 1 of manufacture composition of an organic solvent dispersing element were diluted with distilled water, and were used as the raw material until solid content concentration became 10 % of the weight. 200g of raw materials was paid to 500 cc beaker with which the impeller was equipped. In addition, the "section" means the weight section of the additive at the time of making solid content in a raw material into the 100 weight sections during the following actuation.

[0181] The 0.5 sections (the polyoxyethylene-nonylphenyl ether, HLB:7.8) of surface active agents were added in this raw material, and it agitated by 500rpm for 10 minutes. Subsequently, the 40 sections of 0.1-N sulfuric acids were added in this raw material, and it agitated and neutralized by 500rpm during 10 minutes. The polymer particle condensed by this neutralization. Next, suction filtration of the condensed polymer particle was carried out using the paper filter, most moisture was removed, and the wet cake was obtained.

[0182] After adding the isopropyl alcohol of the 500 sections to this wet cake and carrying out churning washing on a filter, suction filtration was carried out again and the wet cake was obtained. It supplied in the beaker into which n-Deccan of the this wet cake and 120 section was put, and agitated by 500rpm during 30 minutes, and the organic solvent dispersing element which the polymer particle distributed to

n-Deccan was obtained. When the obtained dispersing element was analyzed, moisture content was 0.5 % of the weight, solid content was 44 % of the weight, mean-dispersion particle size was 4 micrometers, and the residue when filtering at a 100-mesh wire gauze was 0.5 % of the weight per solid content.

[Translation done.]